INVESTIGATION OF GAS EQUILIBRIA IN COPPER

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by

Enrique Calixto Chia

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of the Requirements for the Degree

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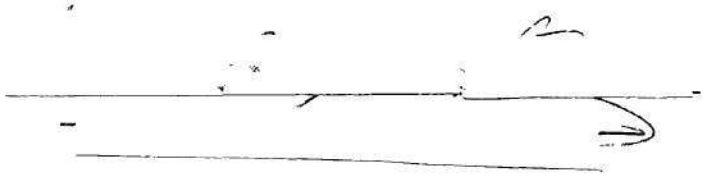

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SUMMARY

The effect of soluble gases, such as hydrogen and water vapor in copper is of importance in the manufacturing of rolled copper. Many of the problems encountered during the hot rolling of chill-cast copper can be directly related to the presence of these soluble gases in the copper.

Hydrogen, which is highly soluble in molten copper, can be harmful if the copper containing it in solution is chill-cast. The solubility of hydrogen in copper sharply decreases at the melting point, thus producing a supersaturated solution of gas in the metal when it is solidified rapidly. While the copper is molten, the excess gases in solution in it will tend to escape as bubbles. However, if the surface of the metal has solidified, these bubbles will not be able to escape, thus producing a porous casting.

A gas analysis apparatus was designed to determine both qualitatively and quantitatively the gases present in the copper. The method used for the analyses was vacuum hot extraction and gaseous absorption. A set of experiments was performed on samples which were melted, doped with different amounts of gases, and chill-cast in the laboratory. Gas losses were studied as a function of time and temperature. The results obtained were in excellent agreement with those predicted by diffusion theory.

A second set of experiments was performed using samples from an industrial rotary furnace which were taken during the reducing cycle. It was found that the steam concentration in the furnace increases at the

beginning of the poling cycle due to the liberation of water during the burning of the green poles. As the cycle continues, the pole ceases to produce steam and a rapid drop in the oxygen and hydrogen content takes place. At the end of the cycle, the pole has become charcoal which will reduce the cuprous oxide present. The resulting low oxygen content will allow more hydrogen to go into solution in the copper which will then cause unsoundness and consequent cracking upon fast solidification and immediate hot rolling.

CHAPTER I

INTRODUCTION

The fact that copper takes gases in solution results in several complications in the production and manufacturing of this metal, causing such problems as unsound and porous castings, hot shortness, and blistering. Exact knowledge concerning the behavior of gas-copper systems is of great importance for the copper producing industry. Since gases in solution in copper influence its electrical conductivity, the gas content is of importance in any copper conductor.

The effects of oxygen, steam, sulphur dioxide, and carbon dioxide encountered during production of copper have been studied and discussed in the literature. However, the effect of hydrogen on the copper is not completely understood.

The properties of copper and the soundness of its castings are affected by occluded gases. The influence of hydrogen on the ductility of copper is generally harmful. Hydrogen can be occluded in copper by mutual contact or chemical reaction with a hydrogen containing compound. The absorption of hydrogen varies according to its bonding conditions, and, like all cases, is more rapid and greater in extent in the nascent than in the molecular state. One of the major causes of a micro- or macro-porosity in castings is the high solubility of hydrogen in copper in the molten condition. Such porosity will produce castings with unsatisfactory mechanical and physical properties.

At room temperature only small amounts of hydrogen are in solution under equilibrium conditions. In solid copper the solubility of hydrogen increases with increasing temperature, and at the melting point a sharp rise in solubility takes place. The temperature-dependent solubility curve is given in Figure 1. In copper, hydrogen appears to be dissolved in the form of protons. It has been proven that this does not effect the normal metal lattice even when hydrogen is present in very high concentrations. Unlike hydrogen, oxygen forms a compound with copper (cuprous oxide) which forms an eutectic at 0.39 percent oxygen. If the oxygen content exceeds 0.18 percent, the oxide eutectic between the pure copper dendrites introduces so much brittleness that the copper cannot be rolled or drawn.

Much work has been done on the absorption of gases by copper and the resulting effects. More knowledge is needed on the exact conditions that determine the amount of absorbed gas in industrial alloys and copper.

The purpose of this investigation is to conduct experiments under controlled conditions in order to provide data on the parameters involved in absorption of hydrogen by copper during production processes.

A study of these data has provided a basis for the design of manufacturing systems which should result in improved working characteristics of the copper produced.

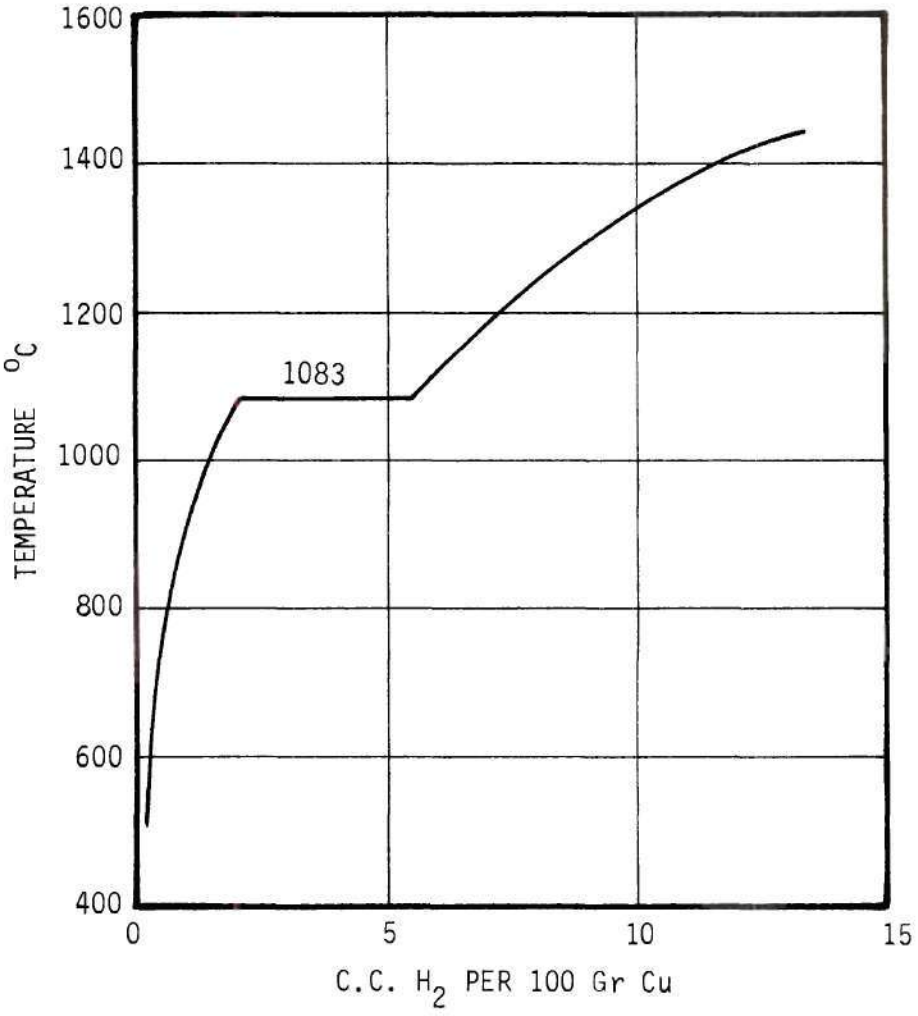


Figure 1. Copper-Hydrogen Equilibrium Diagram at a Pressure of 1 Atmosphere.

CHAPTER II

HISTORICAL BACKGROUND

The earliest investigators to work on the problem of producing sound castings in pure copper were Dick, Stöezel, Von Russel and Mathiessen[1], Caron[2], and Hampe[3]. During the years 1856 through 1876 it was found that hydrogen and sulphur dioxide dissolved in copper. This conclusion was drawn from the appearance and density of ingots cast from metal melted under known conditions. The above mentioned authors also found that nitrogen and carbon dioxide were insoluble in copper. There were conflicting opinions as to the effect of the carbon monoxide.

Guichard[4], Carpenter and Elam[5], Ryder[6], Guillemin and Delachanal[7] analyzed the gases withdrawn from heated solid copper samples under reduced pressures. In every case hydrogen was the predominant gas along with some carbon monoxide, carbon dioxide, and nitrogen. The work of Guillet and Roux[8] confirmed the finding of Guillemin and Delachanal[7] that hydrogen was the main gas evolved from the copper sample. Their measurement of the quantity of hydrogen present was almost in agreement with the solubility measurements found by Iwase[9]. Villachon and Chaudron[10] also determined the solubility of hydrogen in copper and obtained results similar to those of Guillet and Roux[8]. Recent investigators[32] have found that steam reacts with cuprous oxide and that atomic hydrogen from the steam goes into solution with the copper.

Hydrogen

In 1873 W. Hampe[3] stated that it was not known which gas makes the characteristic porous structure of copper when the copper is over-poled. He also stated that there was no doubt that liquid copper was able to take hydrogen into solution. He further stated that copper saturated with hydrogen and kept under another gas which was inert to the copper would give off the hydrogen due to losses by diffusion, producing a sound casting.

G. Newmann and F. Streintz[11], investigating the solubility of hydrogen in copper in 1891, found that copper has the ability to take into solution about $4\frac{1}{2}$ times its volume at N.T.P. Studies made by Bose[12] in 1900 show that the concentration of hydrogen in the metal is given by the exponential power of the partial pressure of the gas, this exponent being dependent upon the number of atoms present in the molecule. In the case of pure hydrogen gas, it would be one-half

$$P = K(p)^n$$

where

P = concentration of hydrogen in metal

K = constant

p = partial pressure

n = exponent .

Where n is one-half for hydrogen gas and one-fourth for methane.

Sieverts and Beckmann[13] found that solid copper wire takes up hydrogen when heated. The pickup of hydrogen up to $400^{\circ}F$ is small; above this temperature it increases with increasing temperature. The absorp-

tion of hydrogen is due to the formation of a solid solution and not to the formation of a chemical compound. It was shown that the solubility of hydrogen increases with temperature for copper, nickel, cobalt and iron. This behavior is not found, however, for palladium, whose solubility decreases with increasing temperature. A series of experiments performed by Sieverts and Beckmann showed that the diffusion rate and pressure dependency of hydrogen occluded in copper can be explained by assuming that molecular hydrogen splits into atoms in both processes. At 930°C the absorbed amount of hydrogen is equal to 1.78 cc. per 100 grams of copper. Figure 1 depicts the temperature dependency of the solubility of hydrogen in copper which increases from 0.19 mg.per 100 g. of copper at room temperature to 1.53 mg. per 100 g. of copper. The solubility at melting point jumps to about three times that of the solid metal.

Sieverts and Krumbhaar[15] in 1910 examined the temperature dependency of the solubility of hydrogen in copper. Results of their work are shown in Figure 2. Table 1 shows the data for this curve. An investigation of the pressure dependency made by them is shown in Table 2.

The temperature dependency of the solubility of hydrogen in copper was thoroughly investigated by Sieverts[16]. He states that at low temperatures diffusion is slow, but as temperature increases the diffusion rate increases rapidly. At high temperatures the hydrogen diffuses through the metal as fast as it would stream in its gaseous phase and therefore equilibrium will occur practically instantaneously. This is especially true for the liquid copper. Roentgen and Moeller[17] also performed experiments on this and found values which were closely related to the former

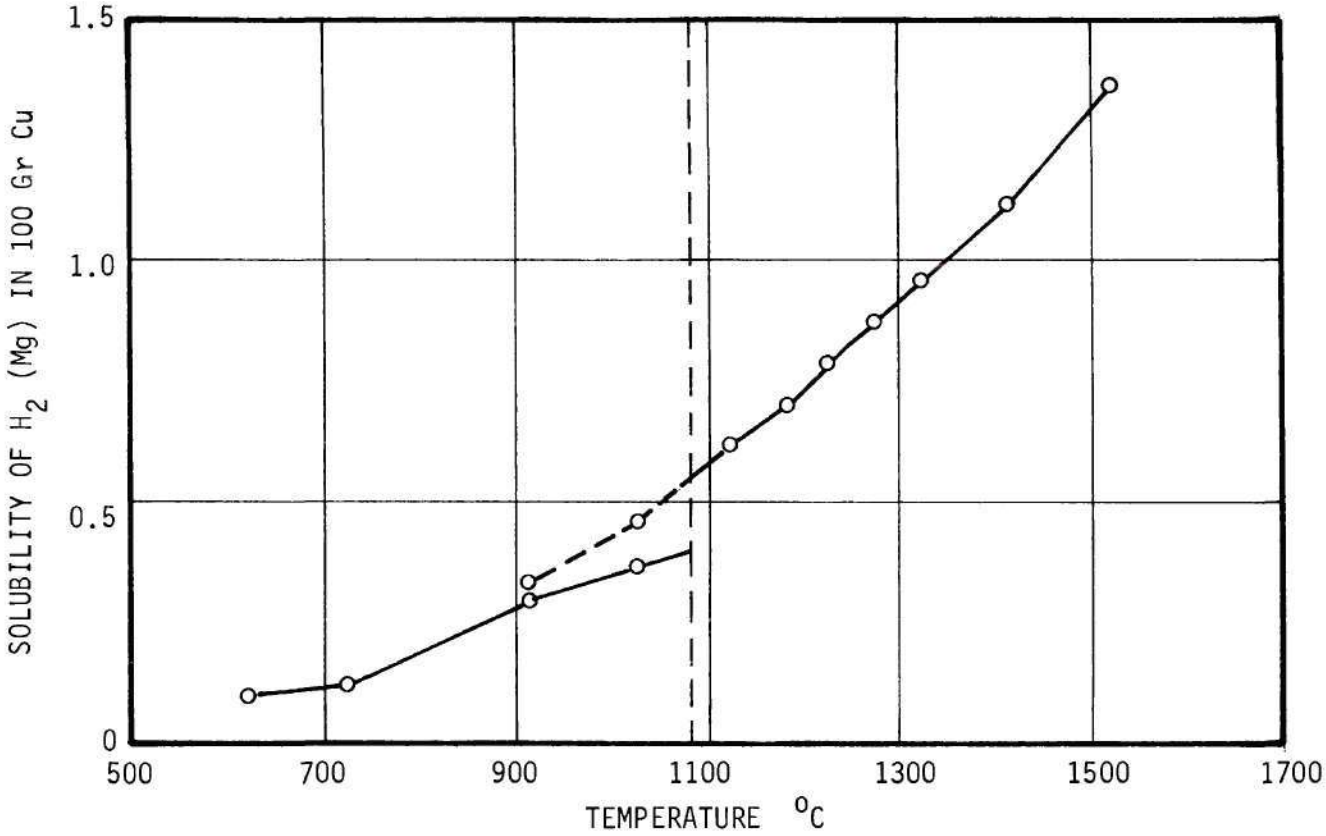


Figure 2. Variation of the Solubility of H_2 in Solid and Liquid Copper with Temperature.

Table 1. Amount of Hydrogen that Goes into Solution in 100 mg. of Solid and of Liquid Copper at Different Temperatures, and Proportion of Hydrogen to Volume of Copper

Temperature, °C	623	725	919	1021	1084	1123	1174	1225	1276	1327	1420	1520
100 gr.solid Cu dissolves mg.H_2	0.08	0.12	0.29	0.36	0.41	---	---	---	---	---	---	---
100 gr.liquid Cu dissolves mg.H_2	---	---	0.31	0.44	0.54	0.61	0.69	0.78	0.86	0.95	1.10	1.35
1 vol.Cu dissolves vol.H_2	---	---	---	---	---	0.60	---	0.77	---	0.94	1.09	1.34

Table 2. Influence of Pressure on the Absorption of Hydrogen

Experimental Temperature: 1123 deg. C.
Weight of copper used: 64.53 gr.

Pressure (in mm Hg.)	mg. of H_2 dissolved by 100 gr. of copper	p/m
1046	0.745	43.5
971	0.705	44.2
883	0.680	43.7
775	0.610	45.1
606	0.549	45.1
403	0.443	45.3
281	0.380	44.2

findings

Much higher solubilities were reported in 1926 by Iwase[3]. By bringing metals and gases together at various temperatures for a sufficient time to obtain equilibrium, he determined the amount of gases absorbed at saturation. Sieverts[16] determinations of the solubilities of gases in metals at different temperatures did not allow sufficient time for the metal and gases to come in contact at each temperature to obtain equilibrium. Consequently, his results do not represent saturated solutions. This, according to Iwase[9], was the reason Sieverts[16] results were lower.

Iwase[3] used an apparatus for his determinations which was a modification of that used by Sieverts[16], as shown in Figure 3. It was found that 100 gms. of copper will dissolved .85 ccs. (N.T.P.) of hydrogen gas each time the temperature of the copper is raised 100°C, and that at a temperature increase of 1000°C copper dissolves 7.7 cc. of hydrogen, as shown in Figure 4. It can be noted from Figure 1 that, at the melting point, the solubility of hydrogen in copper increases from 2 cc/100 g. to 5.5 cc/100 g. Figure 4 indicates that at the melting point the hydrogen content increases from 7.7 cc. to 12.5 ccs. The difference is due to the amount of hydrogen in excess of saturation.

In 1928 the diffusion of hydrogen through copper crystals was studied by G. Tammann and J. Schneider[18] who found that hydrogen diffuses differently along different crystallographic directions, while Coehen[19] pointed out that hydrogen in solution in copper is in the form of protons which are so small compared to the metal atoms that their mobility is unusually great for any type of diffusion. A. F. H. Ward[20] mentioned that

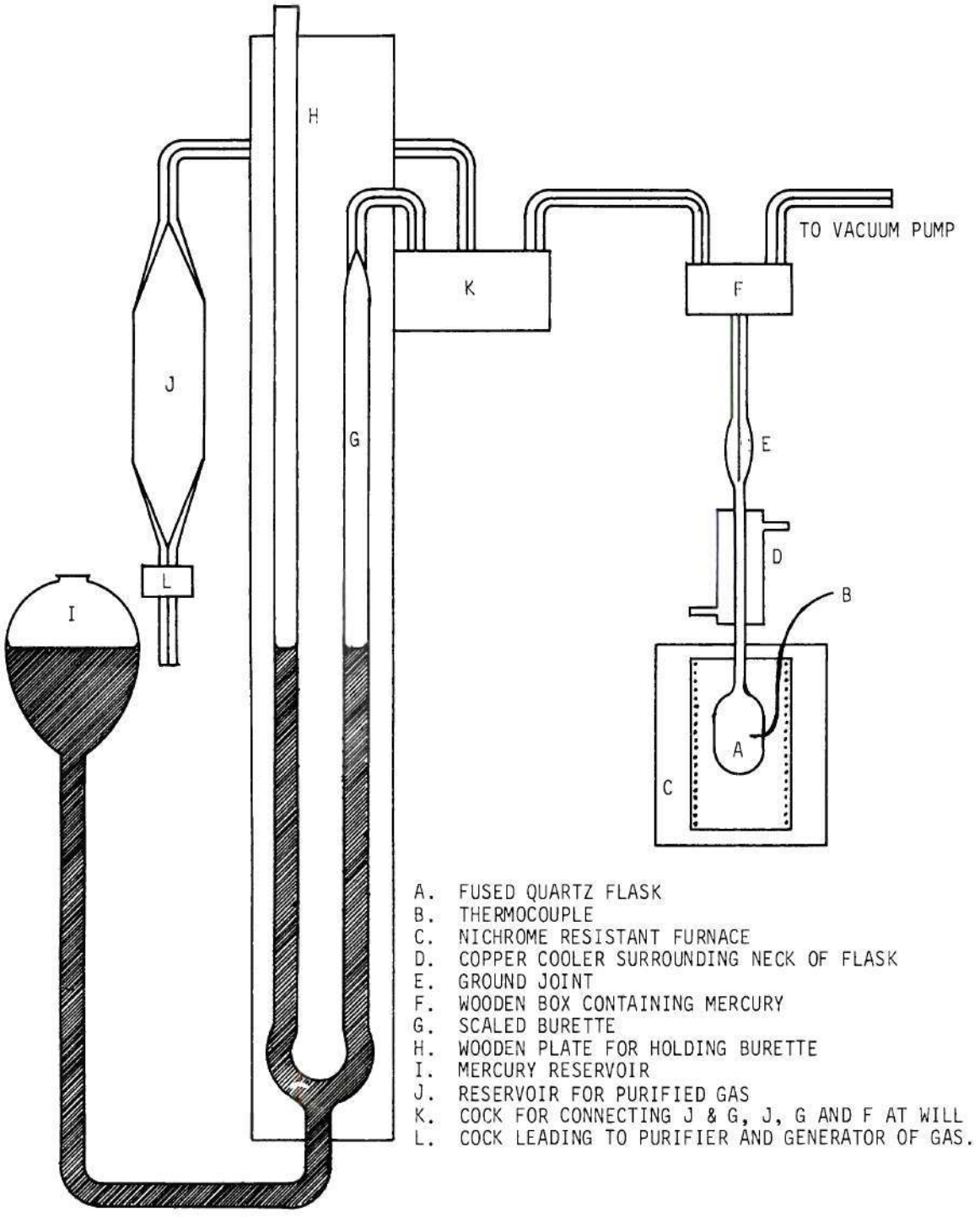


Figure 3. Apparatus for Determination of the Solubilities of Gasses in Metals Used by Iwase in 1926.

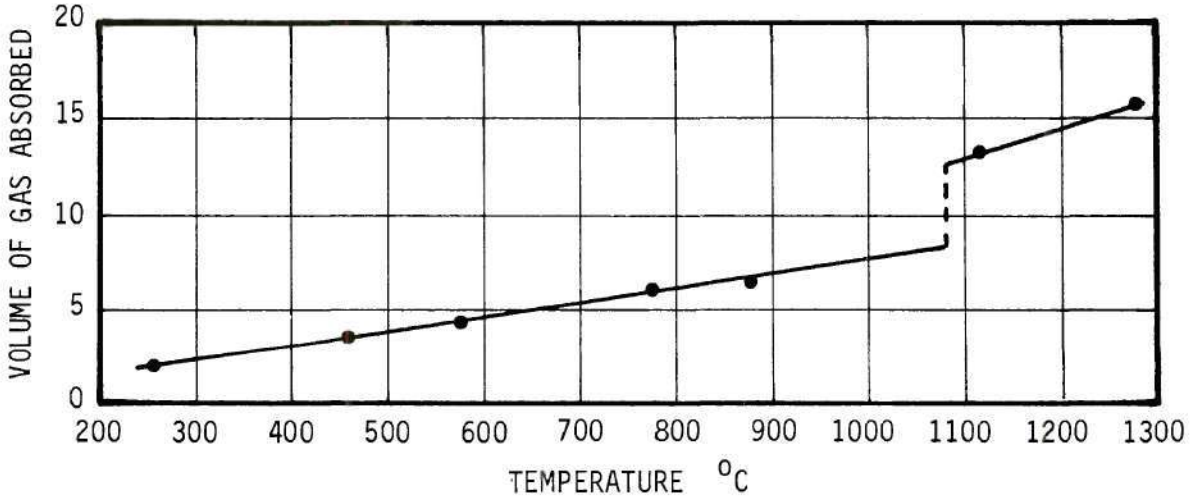


Figure 4. Dependency of Gas Absorption with Temperature.

diffusion can be of two kinds: (a) through the crystals, (b) along the grain boundaries. He also stated that when hydrogen diffuses along the boundaries the probability of forming bubbles and porosity is enhanced. This is the reason why bubbles are usually found at the grain boundaries in a copper structure. Nikuradse and Ulbrich[21] also suggested that the hydrogen present in copper is in the atomic form as long as the hydrogen is in solution. As soon as it precipitates, it forms hydrogen molecules. This was first observed by P. Bardenheuer and Ebbefeld[22] who performed an experiment which consisted of taking electrolytic copper and melting it in a high frequency furnace under very slow melting conditions in order to give the hydrogen an opportunity to escape. They measured the hydrogen content after the copper solidified and cooled down, and it was shown to be 0.012 cc/100 g. of metal. Following this, the same material was again melted and fresh electrolytic copper equivalent to one-third of its weight was added to it. The hydrogen content was then found to be 0.60 cm^2/100 g., an increase of about fifty times over the previous content. The diffusion coefficient of hydrogen in copper was determined by W. Eichenauer and A. Pebler[23] in 1957 and was found to be given by 0.011 exp(-9200/RT). They also studied the solubility of hydrogen in the copper which was determined to be 0.00084 exp(-8600/RT).

G. Borelius[24] performed a very extensive investigation on the solubility of hydrogen in different metals. He studied silver, platinum, copper, iron, nickel, palladium, vanadium, tantalum, titanium, zirconium, thorium, and cerium. He stated that the solubility of hydrogen in these metals increases through the array of these elements. From palladium and on, hydrides, which are metallic chemical compounds, are formed.

These hydrides are rather stable compounds. The elements up to palladium form only solid solutions. Palladium, vanadium, tantalum, and titanium, which take more hydrogen in solution at low temperatures, were found to take so much hydrogen in solution that new phases may be formed. When this happens, the square root of the pressure formula given before is no longer valid. This is especially true for zirconium, cerium, and thorium. Borelius[24] gives as an example of the energy released by combining hydrogen and a metal the 33,000 calories per gram-atom evolving when aluminum takes hydrogen into solution.

In 1929 N. P. Allen[25] found that heating a sample of copper for a long time in carbon dioxide atmosphere progressively caused a decrease in its density. He attributed this to the rise of the oxygen content of the metal according to the reaction $CO_2 + 2\ Cu = Cu_2O + CO$, and not to carbon monoxide in solution. Table 3 shows the different densities of copper melted in various gases. As can be noted from this table, hydrogen lowers the density of copper, producing a casting such as the one shown in Figure 5. This photograph of a copper ingot exhibits hydrogen bubbles. Allen[25] also performed several experiments studying the rate of cooling of the copper ingots. He used a tubular furnace containing a porcelain boat with the sample which was melted and kept in a hydrogen atmosphere. In this experiment, Allen[25] used cathode copper at a maximum of 1200°C. Table 4 shows the effect of the rate of cooling on density. The density of the copper decreases as the rate of cooling increases. Allen[25] also emphasized that the cavities formed in the cast ingot were not spherical but had a trumpet shape beginning at a point near the surface of the ingot and running inward toward the center where they met.

Table 3. Variation of the Density of Copper Melted Under Various Gas Atmospheres

Metal, 50 grm. of cathode copper

Ingot	Gas	Time of Melting	Density
	Hydrogen	10 min.	Below 8.0
	"	10 min.	" 8.0
I	Nitrogen	1 hr.	8.935
M	"	1 hr.	8.935
N	"	3 hrs.	8.934
F	Carbon Dioxide	10 min.	8.917
K	" "	45 min.	8.931
L	" "	45 min.	8.930
B	" "	1 hr.	8.934
C	" "	2 hrs.	8.927
G	" "	3 hrs.	8.927
J	Carbon Monoxide	30 min.	8.942
R	" "	60 min.	8.946
Q	" "	90 min.	8.942

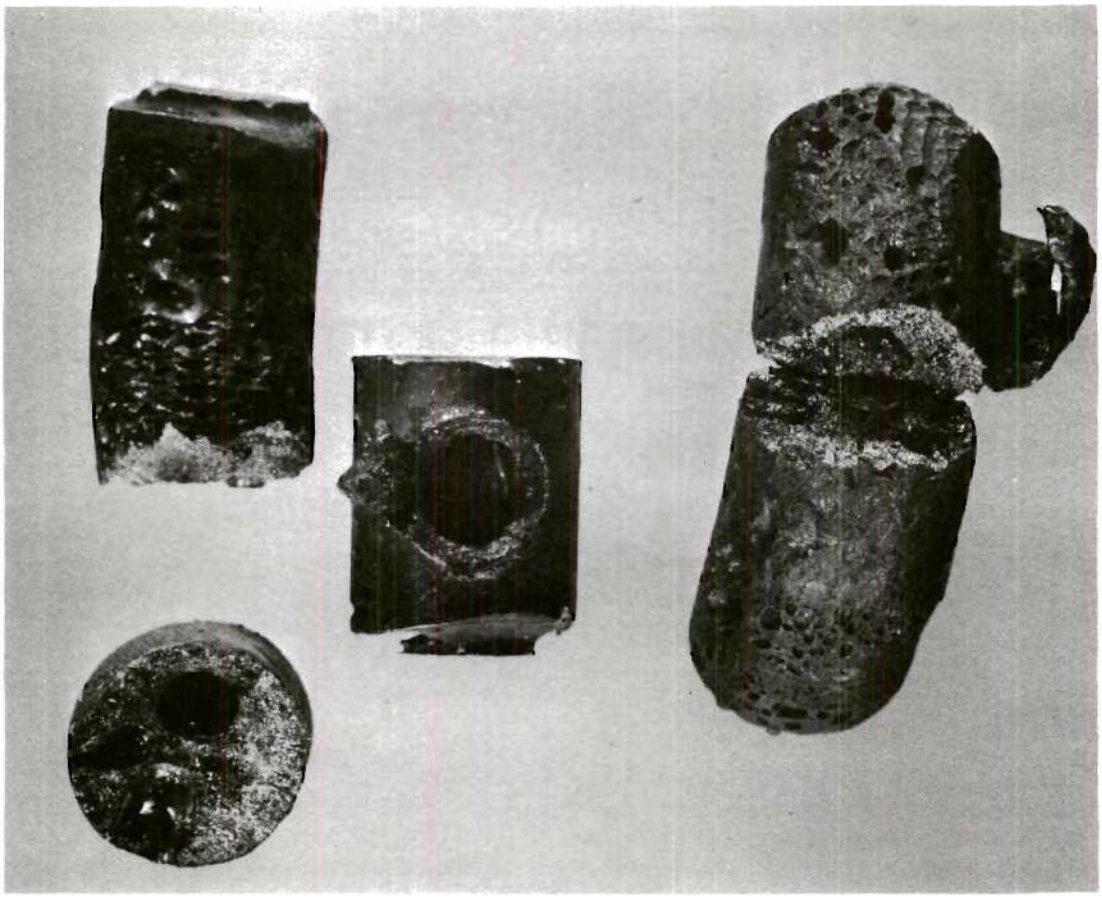


Figure 5a. Photograph of Copper Ingots Exhibiting Bubbles Due to Gas Precipitation.

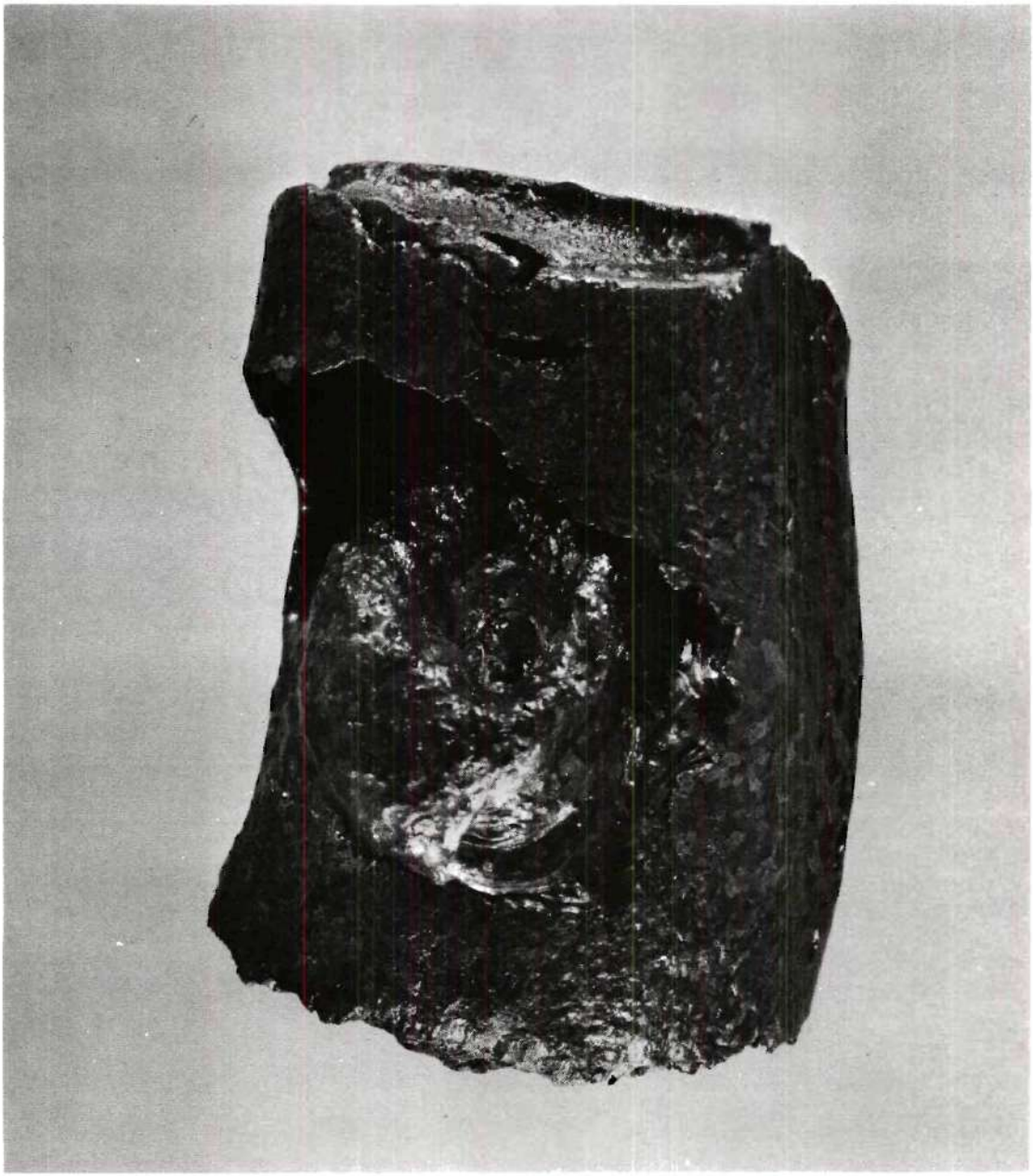


Figure 5b. Photograph of Copper Ingots Exhibiting Bubbles Due to Gas Precipitation.

Table 4. Effect of Rate of Cooling on the Density of Copper

Metal, 60 grm of cathode copper
Maximum temperature, 1200°C. (held throughout experiment)
Atmosphere, Hydrogen

Sample	Time of Cooling from 1110° to 1000°C Minutes	Density
BG	22.0	8.92
BP	15.0	8.91
BD	12.0	8.73
BN	10.0	8.87
BH	6.0	8.82
BI	4.7	8.84
BJ	4.5	8.66
BK	3.5	8.80
BL	Less than 0.5	6.38

The relationship between the rate of cooling and number of blow holes present in a copper ingot was determined and is shown in Figure 6. Allen[25] remarked that in all his experiments which dealt with unsoundness of copper, the type of porosity encountered in commercial copper ingots was never found.

Smithells and Hessenbruch[26] performed experiments with electrolytic copper. According to them, all hydrogen present in the electrolytic copper is given off suddenly when the copper is heated between 450°C and 500°C in a vacuum. At higher temperatures, hardly any hydrogen was given off. They made hardness tests on electrolytic copper which illustrated that when copper was heated to 500°C a significant drop in hardness occurred. This can be attributed to the loss of hydrogen at that temperature. If not annealed, electrolytic copper with hydrogen present was found harder than annealed copper under all degrees of deformation.

W. Hessenbruch[27] performed experiments with various qualities of copper by melting the metal and extracting the gases. These gases were analyzed, and it was found that in some coppers sulphur dioxide was the predominant gas and that in electrolytic copper 40 percent of the total gases present was hydrogen. Table 5 shows the results obtained.

Phillips[28] calculated in 1947 that the hydrogen content of liquid copper increases 50 percent per 100°F rise of temperature. In connection with the dissociation pressure of cuprous oxide, it should be mentioned that this calculated dissociation pressure is that of the oxide phase in equilibrium with the saturated copper melt.

Phillips[28] made studies on the separation of gases from molten copper. He emphasized the reaction between copper and steam and its

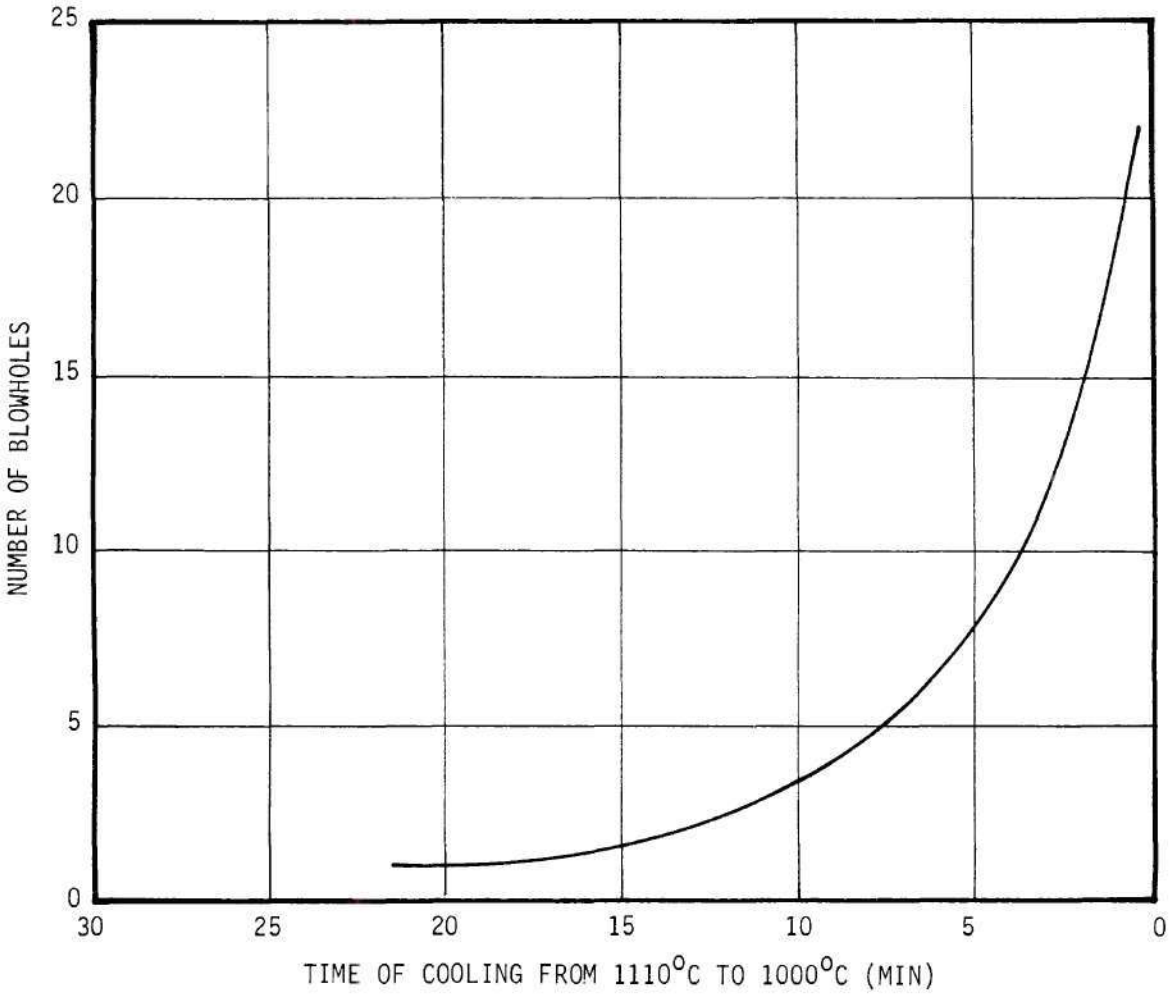


Figure 6. Number of Blowholes in Copper Ingot with Rate of Cooling.

Table 5. Gas Content in Different Qualities of Refined Copper Analyzed by Hessenbruch

Operating Temperature: 1250°C

Sample	Amount of Gas	Volume Percent				H_2	
	$cm^3/100$ g.	SO_2	H_2	CO	N_2	Weight Percent	
1	2.72	58.2	7.9	19.5	14.4	0.00002	Beginning of Casting
2	1.46	85.7	7.4	----	6.9	0.00001	End of Casting
3	1.79	33.9	28.6	37.6	----	0.00005	Beginning of Casting
4	0.73	61.1	11.1	22.2	5.6	0.00001	End of Casting
H	2.81	11.7	35.1	(53.1)	----	0.00009	In H_2 Atmosphere

equilibrium constant. After initial separation of gas, the rate of evolution decreases as freezing progresses. Near the end of the freezing period this rate reaches a value which is similar to the rate of change in volume of the metal as it changes from liquid to solid. If the hydrogen content is initially decreased, smaller amounts of gas will evolve during solidification of the sample. It is also found that the final rate of gas evolution is constant regardless of the hydrogen-oxygen content initially present in the sample. If one changes the amount of oxygen in the liquid metal, the rate of evolution is changed accordingly, but the amount of gas evolution is the same. It is interesting to note that copper with high oxygen content gives off water vapor immediately while copper of low oxygen content first starts to evolve gases when 30 percent of the metal has solidified. It was found that the rate of evolution of this water vapor starts very rapidly.

The effect of hydrogen on the electrical conductivity of copper was first studied by Sieverts[16] in 1913. His experiments consisted of annealing a copper wire at 720°C in a hydrogen atmosphere and measuring its electrical conductivity. The conductivity was remeasured after annealing the same wire at 720°C in vacuum. Table 6 shows increase in resistivity of various metals after hydrogen annealing.

Oxygen

Next to hydrogen, oxygen is of extreme importance to this study in view of the harmful effect of steam formation by the combination of these two gases.

It is known that gas cavities or blow holes appear in copper cast-

Table 6. Increase in Resistance of Different Metals Annealed at 720 deg. C. in a Hydrogen Atmosphere

Temperature: 720 deg. C.
Pressure: 760 mm. Hg.

Metal	Absorbed H_2 p.p.m.	Measured increase in resistance
Pd	77.0	1.8
Ni	6.2	0.14
Fe	1.8	0.04
Cu	0.08	0.01
Pt	0.08	0.002

ings when the oxygen content of the metal falls below certain limits. Therefore, commercial copper should contain just the amount of oxygen necessary to prevent blow holes from appearing and thereby spoiling the properties of the metal.

Bauer and Sachs[29] studied the effect of blow holes in commercially pure copper. They found that these holes can be eliminated by adding, to the melt, elements which have a high affinity to oxygen, thereby deoxidizing the metal.

Prytherch[30] came to the conclusion that blow holes in copper ingots are dependent upon the casting temperature of the metal, the rate of cooling in the mold, and the concentration of the dissolved gas. He improved markedly the quality of copper casting by removing the gases from the molten metal and by keeping a close control on the melting atmosphere.

An interesting theory was presented in 1930 by A. Wells and R. C. Dalzell[31] who found that copper oxide is present in the metal as a colloid during the molten state, and that the surface of the copper oxide is able to absorb hydrogen and carbon dioxide. Figure 7 shows changes in oxygen and sulphur content during blowing and poling as determined by the above authors. The porosity of the copper is correlated with the oxygen and sulphur content. From these curves one can observe that the oxygen content increases from about 0.2 percent to 0.8 percent during the first three hours of the blowing or oxidation process. After blowing oxygen into the metal for three hours, the oxide content is reduced by poling to 0.04 percent O_2. (See Figure 7). At the beginning, the sulphur content is 0.0029 percent and decreases to 0.0019 percent at the end of the first hour of the blowing operation. Thereafter, it decreases to

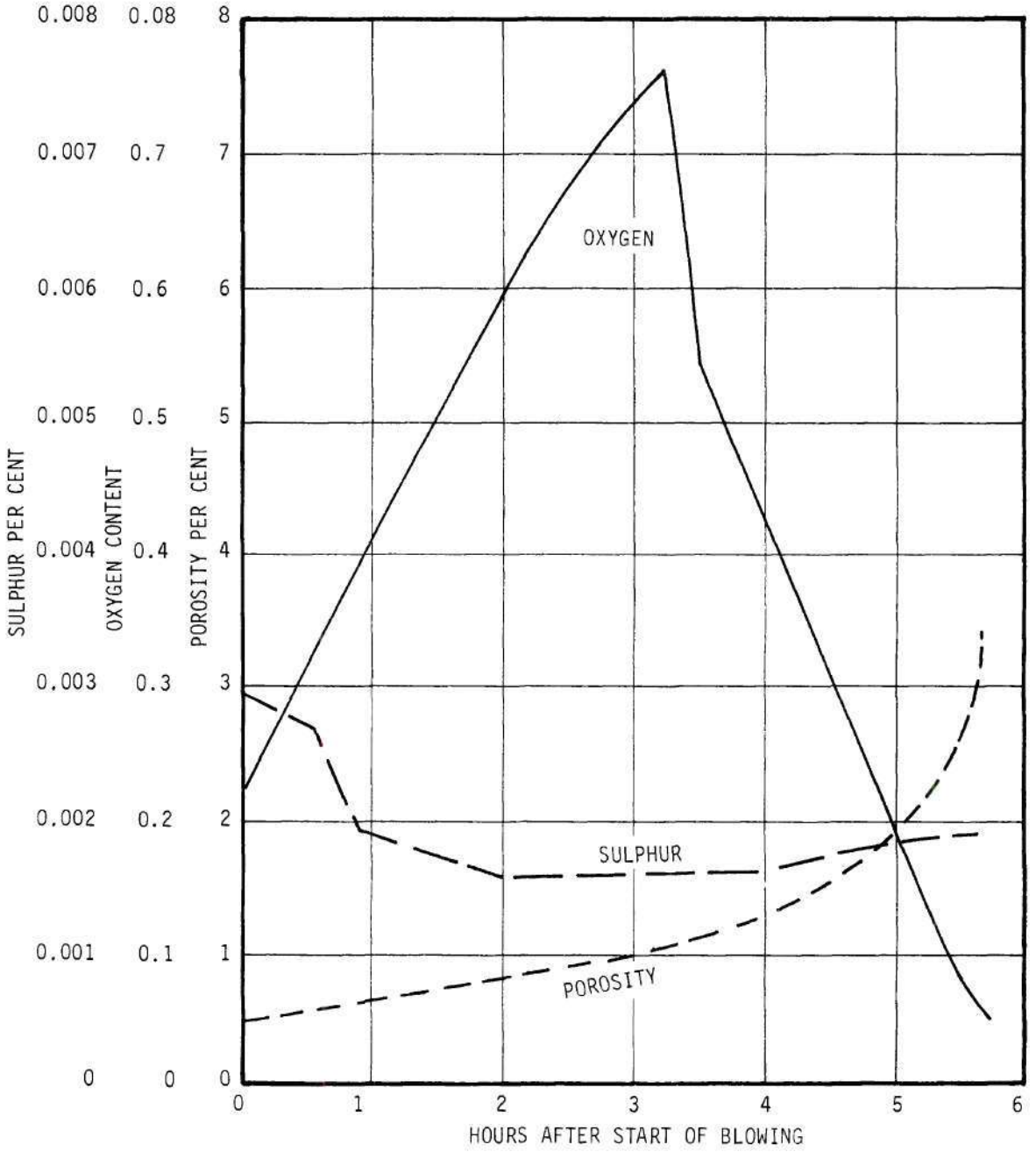


Figure 7. Oxygen and Sulphur Content and Porosity Distribution in Cast Refined Copper.

0.0016 percent, rises again, and approaches 0.0020 percent at the end of the poling period. The porosity of the copper during its refining is depicted in this figure. The porosity percentage of copper starts with less than one percent and increases steadily during the first four hours after blowing. When the operation reaches its fifth hour from the beginning of blowing, the porosity increases rapidly and ends with about 3.5 percent porosity. The porosity content can be easily correlated to the hydrogen content of the copper. Figure 7 shows that during the last hour of the poling operation, the porosity content rises sharply to a maximum of 3.5 percent. This rise corresponds to the sharp rise in the hydrogen content occurring in the copper during the last hour of the poling operation.

Steam

An important topic which deserves consideration in the review of the historical background of gases in copper is seam formation. Hampe[3] was one of the first scientists to become interested in making a study of the generation of steam in molten copper. In studying the over-poling of copper, he found that the porosity in the copper was due to variations in the chemical composition of the molten metal bath. Hampe suspected that some parts of the metal bath contained cuprous oxide in the unreduced form, while other parts were saturated with hydrogen. He believed that these two parts were brought in contact with each other producing a chemical reaction which generated steam during casting. This theory is similar to the one presented in this paper, and much credit should be given to Hampe's work considering the difficulty he had in performing his

experiments using the techniques available sixty years ago.

The reaction between oxygen and hydrogen in solid copper causes severe damage to the metal. In 1902 Heyn[33] made some experiments in this field. He found that when copper is heated in the presence of hydrogen, the oxygen contained in it in the form of cuprous oxide will react with the hydrogen, and steam will be generated within the metal causing internal cracking.

In 1932, Allen and Hewitt[32] carried out experiments to study the effect of the water vapor content of the furnace atmosphere on the hydrogen content of the metal. The effect of the oxygen content of the copper on the equilibrium constant was thereby determined. They found that for any water vapor pressure the quantity of hydrogen present in equilibrium rose progressively as the oxygen content of the copper decreased. From these results they concluded that the oxygen content was inversely proportional to the square of the hydrogen pressure. They obtained a straight line when they plotted the logarithm of the oxygen content of the saturated solution against the logarithm of the observed hydrogen pressure. Allen and Hewitt also studied the effect of temperature on the reaction between steam and molten copper and found that as the temperature increased, the hydrogen content of the melt also increased. During this study the melt was kept in equilibrium with an atmosphere of a known steam content.

Carbon Monoxide

In addition to the experiments with steam in molten copper, Hampe[3] also made studies on the effect of carbon monoxide in molten copper. He

believed that carbon monoxide would not blister the copper but would cause only a slight lowering of its density. However, Dick[34] found that if the copper was solidified in carbon monoxide atmospheres, the ingot resulting would have a high density. At the same time, Caron believed that the carbon monoxide would cause the copper to spit and blister during the casting operation.

Sulphur Dioxide

Another gas which causes blisters, bubbles, or porosity in general, and has been subject to prolonged discussions during many years, is sulphur dioxide. In 1876, Bottger[35], a Russian scientist, examined the causes of this porosity and came to the conclusion that sulphur dioxide caused it. Many publications have presented this viewpoint in the past, and is still a popular idea today.

In 1918, Skowronski[36] performed many experiments on the unsoundness of the copper produced by sulphur dioxide. He stated that copper which has been excessively reduced during the poling period of the refining process is unfit for commercial purposes due to its excessive porosity. In order to study the relationship of sulphur to the over-poling of the metal, Mr. Skowronski took cathode copper with a negligible sulphur content and attempted to overpole the melt by poling with green wood. The copper could not be over-poled, and all cast bars showed a "level" set and proper "pitch". He concluded that "level set" or "tough pitch" copper was obtainable without oxygen, and that the over-poling of the copper cannot be considered as a result of lack of oxygen.

CHAPTER III

REVIEW OF INDUSTRIAL REFINING AND CASTING OF COPPER

Copper must be refined since crude copper is too impure to be used directly. Crude copper contains large amounts of antimony, iron, arsenic and bismuth and recoverable quantities of silver and gold.

Copper can be refined by electrolysis or by pyrometallurgy. Generally, electrolytic refining is used only when the amount of precious metals warrants this expensive method.

The fire refining operations may be divided as follows:

A) Charging the metal

B) Melting

C) Oxidizing or Blow

D) Reducing or Poling

E) Casting

Usually all operations take about twenty hours to complete a full furnace cycle.

Crude copper usually is supplied to the refinery in the form of cathodes or ingots. They are charged into the furnace mechanically. A typical machine takes a pile of thirty cathodes weighing close to 6,000 pounds at a time and puts them in the furnace compactly. Charging time for a furnace is usually two hours. Melting begins once the furnace is charged. The doors are closed and fire is increased to hasten melting of the copper which requires about ten hours.

After the load of the furnace is molten, the next step is the oxidation or "blowing". This operation is accomplished by blowing air through pipes inserted through the doors of the furnace. As this is done, the impurities present in the copper are oxidized and they escape with the flue gases or enter the slag. Large amounts of impurities are oxidized by exposure of the molten surface to air. This reduces the total time required for the oxidation of the impurities.

The slag formed on the surface of the molten metal is skimmed off; this is done two or three times during blowing, depending on the amount of impurities oxidized. The bath is then covered with a clean, molten layer of cuprous oxide. The blowing operation comes to an end when the copper reaches an oxygen content of 0.8 or 0.9 percent (8 to 10 percent of cuprous oxide). This is determined either by microscopic investigation of the amount of cuprous oxide eutectic, or by fracturing a sample. If the fracture has a brick red color and is crystalline and brittle, the copper is saturated with oxygen. It is called "set" copper and contains about 0.90 percent oxygen, depending upon the temperature of the molten metal. At this point the copper is ready for the poling operation.

Poling consists of thrusting green hardwood poles into the molten bath, which reduces the cuprous oxide content to the proper amount.

The heat coming from the bath causes destructive distillation of the wood in which hydrocarbons, carbon monoxide, hydrogen and water vapor are evolved. Carbon monoxide and hydrogen reduce the cuprous oxide to copper, and the rest of the gases, in their evolution, agitate the bath and speed up the reactions involved. Frequent samples are taken to determine the degree of reduction processes. Once the desired reduction stage

has been obtained the fracture shows a rose-colored metallic luster, with fine radial crystals. This copper is called "tough pitch" because within characteristic composition limits, the metal has maximum malleability and ductility. When the desired stage of reduction has been reached, the surface of the copper is covered with a layer of charcoal, in order to keep the metal at the desired composition until it is ready to be poured. Deoxidation is not complete in tough pitch copper as it contains about 0.03 percent oxygen. The copper is then ready for casting into wire bars, commercial shapes, cakes, billets and ingot bars. Wire bars are cast into copper molds which are sprayed with a calcium carbonate suspension in water. The molds are placed radially on a circular casting machine known as the "clark wheel". As the wheel turns, the molds are filled with molten copper from the furnace. Once the copper has set, these molds tip automatically, dropping the bars into a water bath from which they are removed by means of a conveyor belt.

Chemistry of Fire Refining

In fire refining, the atmospheric oxygen oxidizes the copper, and the cuprous oxide thus formed acts as a vehicle to carry oxygen into the molten metal, thus eliminating some of the impurities.

During blowing the following reactions take place:

$$4\ Cu + O_2 = 2\ Cu_2O$$

$$Cu_2O + SiO_2 = Cu_2O \cdot SiO_2$$

$$5_2Cu\ O_2 + 2\ As = As_2O_5 + 10\ Cu$$

$$As_2O_5 + Cu_2O = Cu_2O \cdot As_2O_5$$

$$5\ Cu_2O + 2\ Sb = Sb_2O_5 + 10\ Cu$$

$$Sb_2O_5 + Cu_2O = Cu_2O \cdot Sb_2O_5$$

$$2\ Cu_2S + 3\ O_2 = 2\ Cu_2O + 2\ SO_2$$

During poling the following reactions take place in the bath:

$$Cu_2O + C = 2\ Cu + CO$$

$$2\ Cu_2O + C = 4\ Cu + CO_2,$$

and in the furnace atmosphere,

$$Cu_2O + CO = 2\ Cu + CO_2\ .$$

Poling of the metal is continued until the copper contains as little as 0.035 or 0.04 percent oxygen. The arsenates, antimonates and silicates will form a slag with an excess of Cu_2O. These will go to the surface of the melt and are slagged off after the blowing operation is finished. It may happen that some of these compounds form sluggishly or ascend slowly. If this is the case, final slagging should be delayed until the impurity content does not decrease further.

Sulphur and carbon form gases which go into solution in the metal to a certain extent. The excess of these gases will be, however, removed readily.

CHAPTER IV

THEORY

The production of insoluble gases which can cause unsoundness of copper ingots arises from the reaction of cuprous oxide with hydrogen, copper sulfide, and carbon monoxide according to the following reactions:

(1) $2H + Cu_2O = 2\ Cu + H_2O$,

(2) $Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2$,

(3) $CO + Cu_2O = 2\ Cu + CO_2$.

The products of these reactions, H_2O, SO_2, and CO_2 are very slighly soluble or insoluble in solid copper and will therefore either precipitate out as gases during solidification or remain in super-saturated solution. The second reaction could cause unsoundness in copper produced by older practices in which copper contained substantial sulphur impurities, but it is known that unsoundness develops in modern sulphur-free copper. The third equation is unlikely to take place because until now there was no evidence of the solubility of carbon monoxide in copper. In fact, sound OFHC copper is produced under CO atmosphere. Therefore, the equation showing the reaction between hydrogen and cuprous oxide seems the most probable as a logical explanation of this phenomenon.

The hydrogen reaction is reversible and the equilibrium constant increases with temperature. Consequently, the hydrogen content in equilibrium is less as the temperature decreases. Metallographic investigations of copper ingots show that blow holes are at the grain boundaries

between primary dendrites of copper, especially where the metal is last to solidify. This is because the metal becomes richer in oxygen as it is poured into the mold, forcing the above reaction to proceed in the direction favorable to the formation of steam.

As long as the copper is still liquid, the gases formed are free to escape through bubble formation and escape. However, when the copper solidifies the gas solubility in copper decreases significantly and large amounts of gas may be liberated or remain entrapped inside the casting either as blow holes or in supersaturated solution. Blow holes appearing between primary dendrites are caused by this entrapping process of free gas.

During the solidification, where solid and liquid coexist, steam that forms is no longer free to escape completely. Consequently, the metal rises above the level of the mold under slow cooling conditions in normal casting practice. This is due to the pressure of the entrapped gases. Hydrogen by itself may be responsible for the formation of micro or macroporosity in many instances; However, steam formation liberates more free energy and, consequently, steam can exert a higher gas pressure than hydrogen alone. Hydrogen, when combined with oxygen, can produce more micro and macroporosity in the solid copper.

It is apparent that hydrogen is the primary cause of bubble formation either as hydrogen or steam. To form free hydrogen only two relatively fast moving hydrogen atoms have to join at the surface of a grain or a bubble. To form a water molecule, a relatively immobile oxygen atom must free itself from combination with two copper atoms and join two hydrogen atoms. This process is slower and therefore is almost suppressed in

solid state. However, free hydrogen may react with oxygen at the copper surface and form water molecules.

A gas bubble, which is composed of a mixture of hydrogen and steam, will have a gas content that will depend on the analysis of the copper metal, the temperature of precipitation and the time it is held at each temperature.

Figure 5(A) and (B) and the following micrographs demonstrate the gas damage to the copper metal when it is slow-cooled and fast-cooled. Figure 5(B) shows a copper ingot containing gases which was slowly cooled. Part of the metal which was still liquid was blown out of the ingot producing large cavities. Figure 8 demonstrates the gas bubble formation under fast solidification as it occurs in chill casting. Bubbles are formed in the last solidifying metal between the solid dendrites and, therefore, appear along the grain boundaries. Under fast cooling the copper becomes supersaturated with gas which tends to precipitate out. This process will be accelerated by stresses as they are applied in the hot rolling immediately after casting in the chill casting. Hence, close arrays of bubbles are formed along the grain boundaries as demonstrated in Figure 9, which shows such bubble formation in a rolled structure. The string of bubbles shown is the continuation of a crack. Figure 11 shows two copper ingots with different hydrogen contents. Both were cold rolled to the same degree of deformation.

Even without rolling, gas bubbles will grow in the solid chill cast copper. This is demonstrated in Figure 10 where slip lines can be seen around the bubble indicating that this bubble has been formed or at least has been growing in the solid state. Gas pressures of several

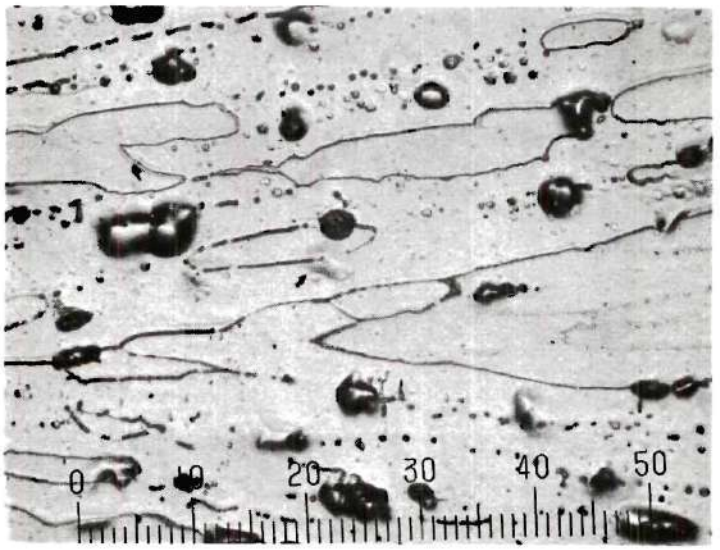
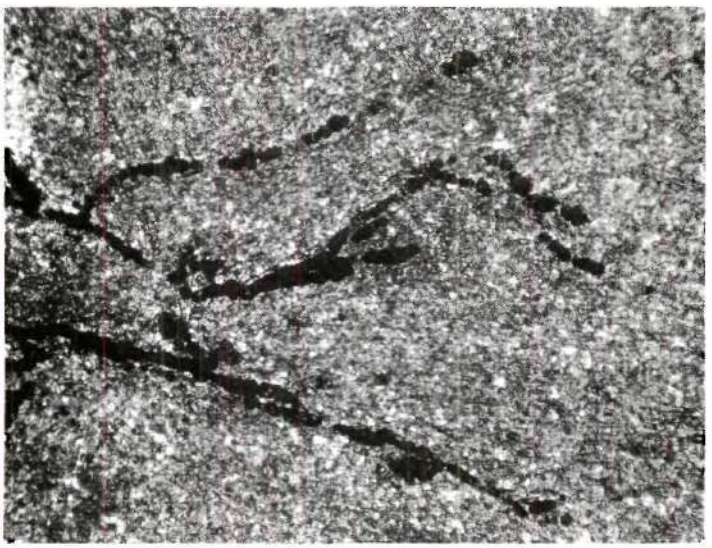
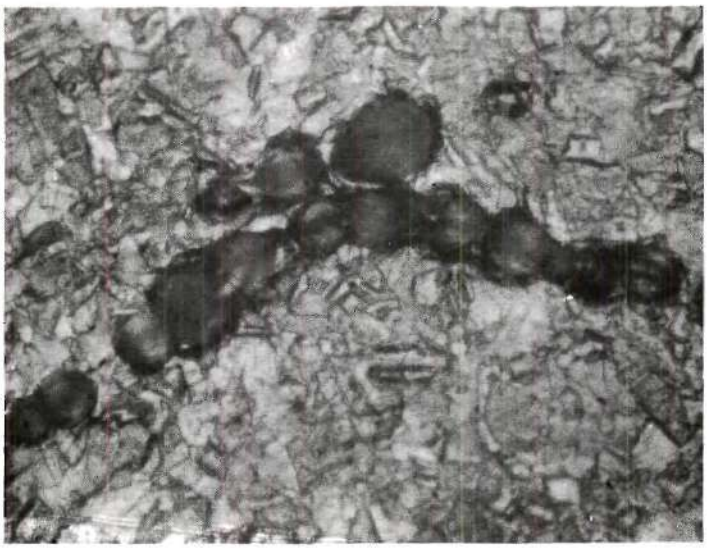


Figure 8. Gas Bubble Formation Under Fast Solidification.



(a) 75X



(b) 800X

Figure 9. Array of Bubbles in a Rolled Structure.

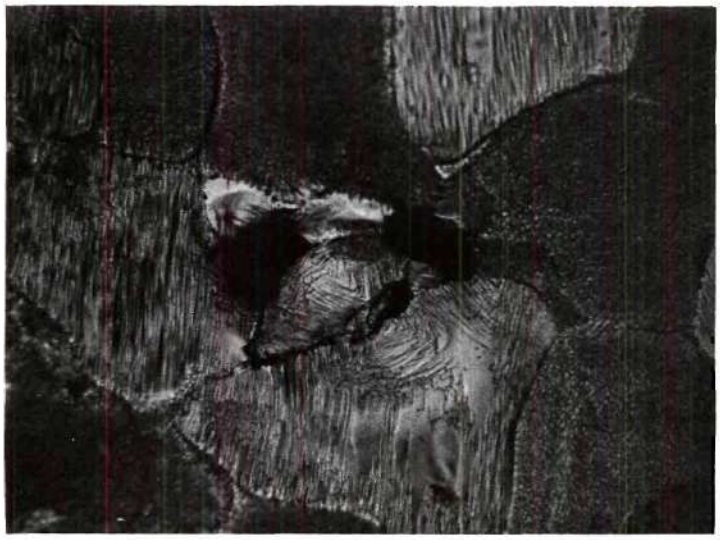
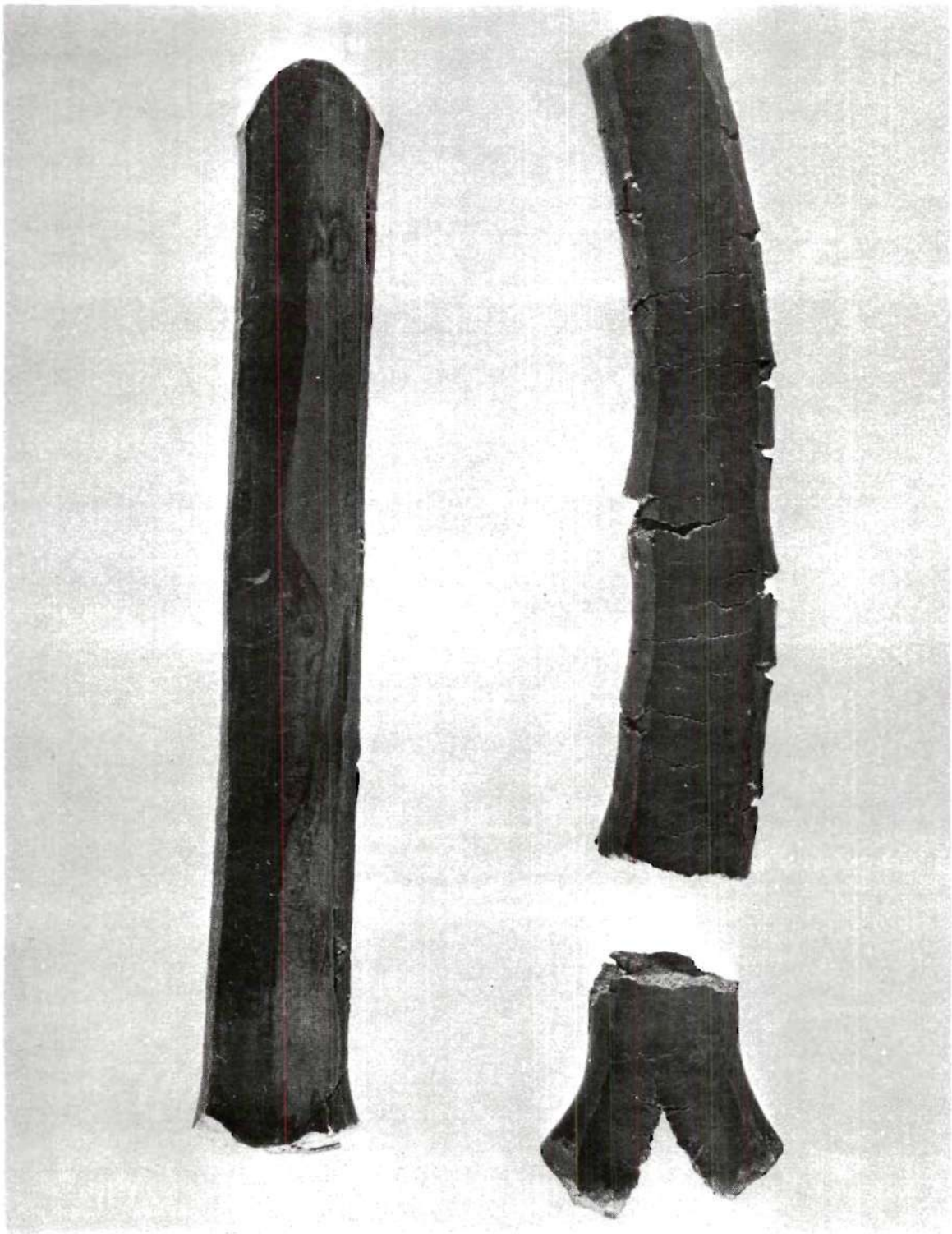


Figure 10. Photomicrograph Showing Clip Lines Around the Gas Bubbles.



(a)
HYDROGEN CONTENT = 0.19 c.c./100g.

(b)
HYDROGEN CONTENT = 2.6 c.c./100g.

Figure 11. Photograph Showing Two Copper Ingots Rolled to Same Degree of Deformation.

thousand atmospheres can develop due to gas precipitation.

As it has been pointed out previously, the reaction

$$2H + Cu_2O = 2\,Cu + H_2O$$

is reversible, and consequently the absorption of water vapor by the molten metal may be accompanied by the formation of atomic hydrogen, which goes into solution in the copper at a considerably faster rate than the hydrogen in the molecular state. One could say that the direction in which this reaction will proceed will be controlled by the pressure and temperature conditions.

The pressure dependence of hydrogen on its solubility can be expressed as follows:

$$\text{Solubility of gas} = K\sqrt{P}\ , \qquad (4)$$

where

K = constant, and

P = external pressure of hydrogen exerted by the gas.

The hydrogen present in the metal thus will be proportional with the square root of the hydrogen pressure in the atmosphere in the furnace. The same exponential power applies for the oxygen pressure with a different constant. The oxygen concentration is directly proportional to the cuprous oxide concentration. With a low hydrogen pressure at liquid metal temperature, fairly high pressures can develop at lower temperatures. This is especially true in the solid state because of the decrease of solubility with temperature. For example, if the hydrogen pressure is one-tenth of an atmosphere at 1300°C, it will exceed one atmosphere at 900°C (see Figure 7).

Most hydrogen, however, originates from dissociation of steam. This means that the dissolved hydrogen is essentially in equilibrium with the steam present in the furnace atmosphere. Consequently, one can have at the same time hydrogen and oxygen present in the same melt. The formation of either product depends exclusively on how the melting process is conducted.

The equilibrium constant for Equation (1) can be written as follows:

$$K = \frac{(C_H)^2 \cdot (C_O)}{(C_{Cu}) \cdot (C_{H_2O})} \tag{5}$$

where

C_H = concentration of hydrogen

C_O = concentration of oxygen

C_{cu} = concentration of copper

C_{H_2O} = concentration of water vapor

The concentration of copper is considered unity, so

$$K_1 = \frac{(C_H)^2 \cdot (C_O)}{(C_{H_2O})} \quad . \tag{6}$$

The following values are taken from a poling experiment, number two, 80 minutes after starting of the poling;

C_H = 2.25 cc./100 gr.,

C_O at 0.03% = .21 cc./100 gr.,

C_{H_2O} is not known and set to be X.

The constants then yield:

$$K_1 \cdot X = (C_H)^2 \cdot (C_O) = .4725 \quad . \qquad (7)$$

Since K_1 can be considered a constant, the product of the hydrogen concentration and the cuprous oxide concentration indicates the steam concentration X. The variation of the steam concentration over the poling process is demonstrated in Figure 30. Since K_1 is temperature dependent and the temperature drops during the poling operation, Figure 32 contains the combined effect of temperature and steam concentration.

Provided the temperature and the steam concentration are kept constant, Equation (5) reduces to

$$(C_H)^2 \cdot (C_O) = K_2 \qquad (8)$$

where K_2 is .0162 at the end of the poling process.

With high oxygen content, the hydrogen concentration therefore must be low, and at low oxygen content the hydrogen concentration must be high, as shown in Table 7.

The foregoing theory demonstrates the laws governing the gas-metal equilibria in copper. Oxygen alone will not cause damage to the casting, or produce unsound casting; however, hydrogen will cause unsoundness, either alone or in combination with oxygen in the form of water vapor.

Table 7. Variation of the Concentration of Hydrogen and of Cuprous Oxide Under Equilibrium Conditions

C_{H_2}	C_{Cu_2O}
12.7	0.001
5.65	.005
4.02	.010
2.85	.020
2.32	.010
2.00	.040
1.79	.050
1.27	.100
.4	1.000

CHAPTER V

PREPARATION OF SPECIMENS FOR GAS ANALYSIS

In order to study the gas content of the metal in gas-metal reactions, specimens were prepared in which gases were charged artifically into the melt. These specimens were cast in a quench mold so that all the gases in solution in the liquid metal would be trapped in solid state.

Charging of Melts with Gas in the Laboratory

Samples for the determination of gases in the copper were melted and charged with different proportions of gases in order to study their behavior under different conditions. The copper used for these sets of experiments was electrolytic copper, 99.96 percent pure, with the following impurities:

Oxygen	0.03%
Tin	0.0003%
Lead	0.0002%
Bismuth	0.0004%
Chromium	0.0002%
Manganese	0.0001%
Silver	0.0006%
Gold	0.00001%
Iron	0.0008%
Nickel	0.0004%
Arsenic	0.0003%
Antimony	0.0002%

The copper wire was wound into small coils one-inch in diameter and

placed in a ceramic crucible. The setup used is depicted in Figure 12. For melting the copper, a high frequency induction furnace, A, made by Lepel was used. The crucible, B, consists of a bottom part and a top part that has an aperture for the gas to be introduced into the melting atmosphere. Care was taken that no leakage of gas existed between the top and bottom crucible. C and D are bottles of methane and hydrogen gas, respectively, with flow rates regulated by meters at E and E'.

Every heat consisted of one pound of metal, and no additions were made to the melt. The copper was melted under various gas-air ratio atmospheres and held for 15 minutes after the metal was molten in order to obtain equilibrium. The gas used was natural gas (CH_4) mixed with different proportions of air. Air for the mixture was regulated by using a flow rate meter at G.

Once equilibrium had been obtained, the metal was poured into a copper mold 3-inches long, 2-inches outside diameter with an aperture of 1/2-inch diameter, 2-inches long, and was quickly quenched after solidification took place. In this process a supersaturated solution of gases in the copper was obtained. The copper sample was cut into slices of about 10 grams each and the surface oxide was filed off.

Gas Losses During Storing of Samples

A set of experiments was performed to determine the effect of temperature and time on the amount of hydrogen lost by diffusion. These experiments were performed mainly to perfect the handling of the samples after taking them from the furnace. A melt was prepared under a three-to-one gas-air atmosphere. Twenty samples were poured into a copper mold

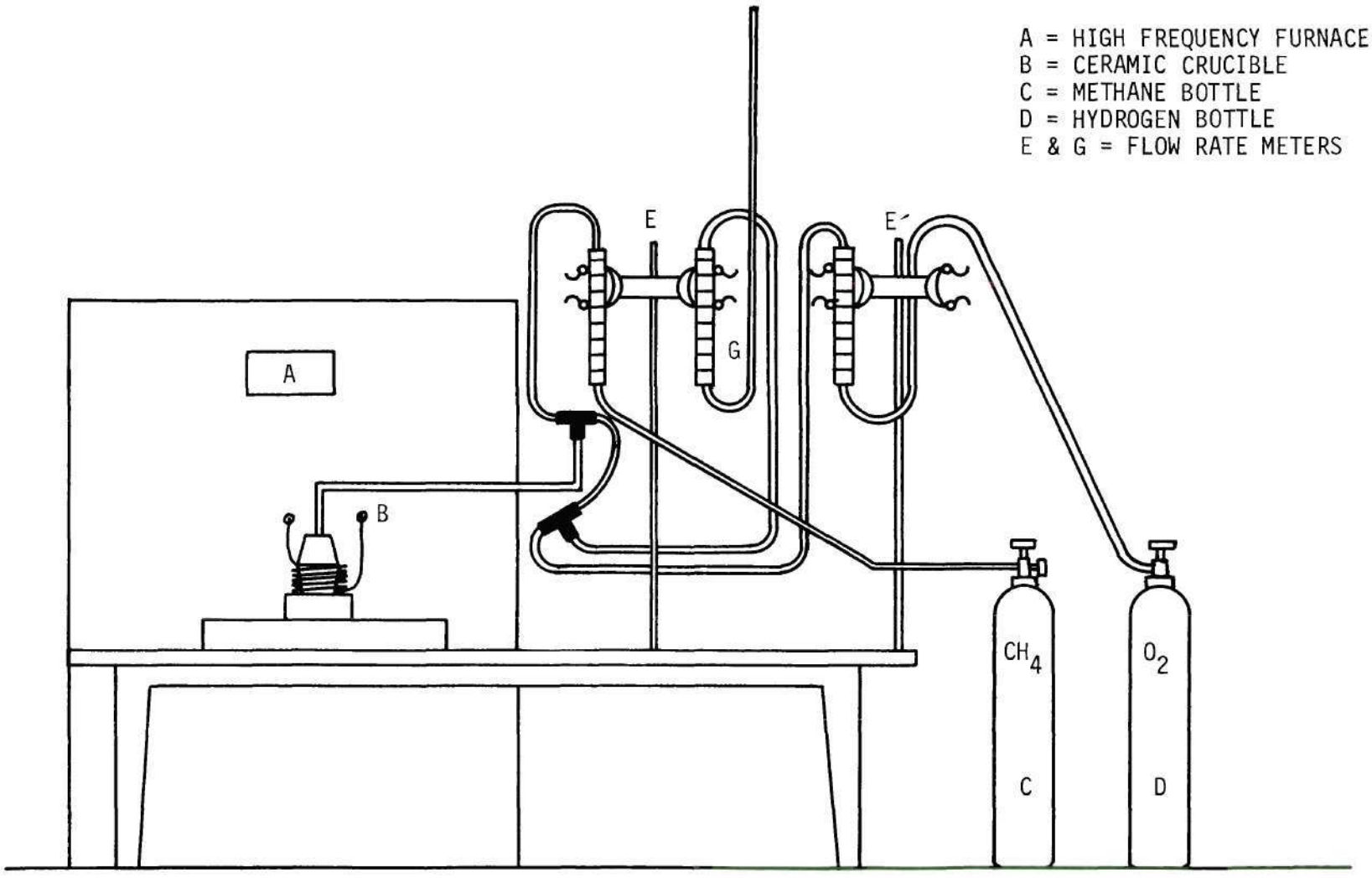


Figure 12. Schematic Diagram of the Melting Furnace and Gas Charging Apparatus.

Figure 13. High Frequency Induction Melting Furnace and Related Equipment.

(for fast chilling) and immediately submerged in carbon dioxide snow. One of these samples was analyzed immediately after solidification while the rest of them were divided into four groups. Four samples were placed in carbon dioxide snow. Four more were placed on a shelf at room temperature. Another four were placed in a furnace at 200°F, and the last seven were placed in a furnace at a temperature of 400°F. A sample from every set was removed from its environment every four days and analyzed for hydrogen, oxygen, and total gas content. Results from these experiments are given in Table 8 and plotted in Figure 20. It was found that the samples stored in carbon dioxide snow kept practically all their original hydrogen content they had in solution. The samples kept in the furnace at 400°F lost nearly all their hydrogen content. At the end of the sixteenth day the hydrogen content of the sample kept at 200°F was almost the same as that kept at 400°F. Little loss of hydrogen was found to take place in the samples kept at room temperature.

Sampling of Copper from the Industrial Furnace and the Influence of Cooling Velocity on Microstructure

In the industrial furnace, copper is sampled by dipping an iron ladle into the molten metal and pouring the ladle specimen into an iron mold. This sampling operation presents such difficulties as follows.

Nonhomogeneity of the molten metal in the furnace will produce an erroneous value of the amount of oxygen present in the copper. This may be due to furnace atmosphere, slag on the metal, refractory of the furnace, and pole reactions. In order to investigate whether the molten bath is homogeneous, five or six samples should be taken at the surface at different places in the furnace as shown in Figure 10. A second test

Table 8. Hydrogen and Total Gas Content Obtained from Copper Samples Melted Under a 3-1 Gas-Air Ratio

Samples melted under atmosphere composed of 3 gas - 1 air ratio

Poured in copper mold

	Room Temp.		CO_2 Snow		200°F		400°F	
	Total	H_2	Total	H_2	Total	H_2	Total	H_2
As cast	0.085	0.0229						
2 days	0.085	0.0217	0.06	0.0226	0.0844	0.0149	0.071	0.0106
4 days	0.0790	0.0210	0.048	0.0224	0.0781	0.0118	0.080	0.0088
6 days	0.077	0.0209	0.075	0.0229	0.050	0.0101	0.0755	0.0079
8 days	0.080	0.0192	0.074	0.022	0.076	0.0075	0.069	0.0070

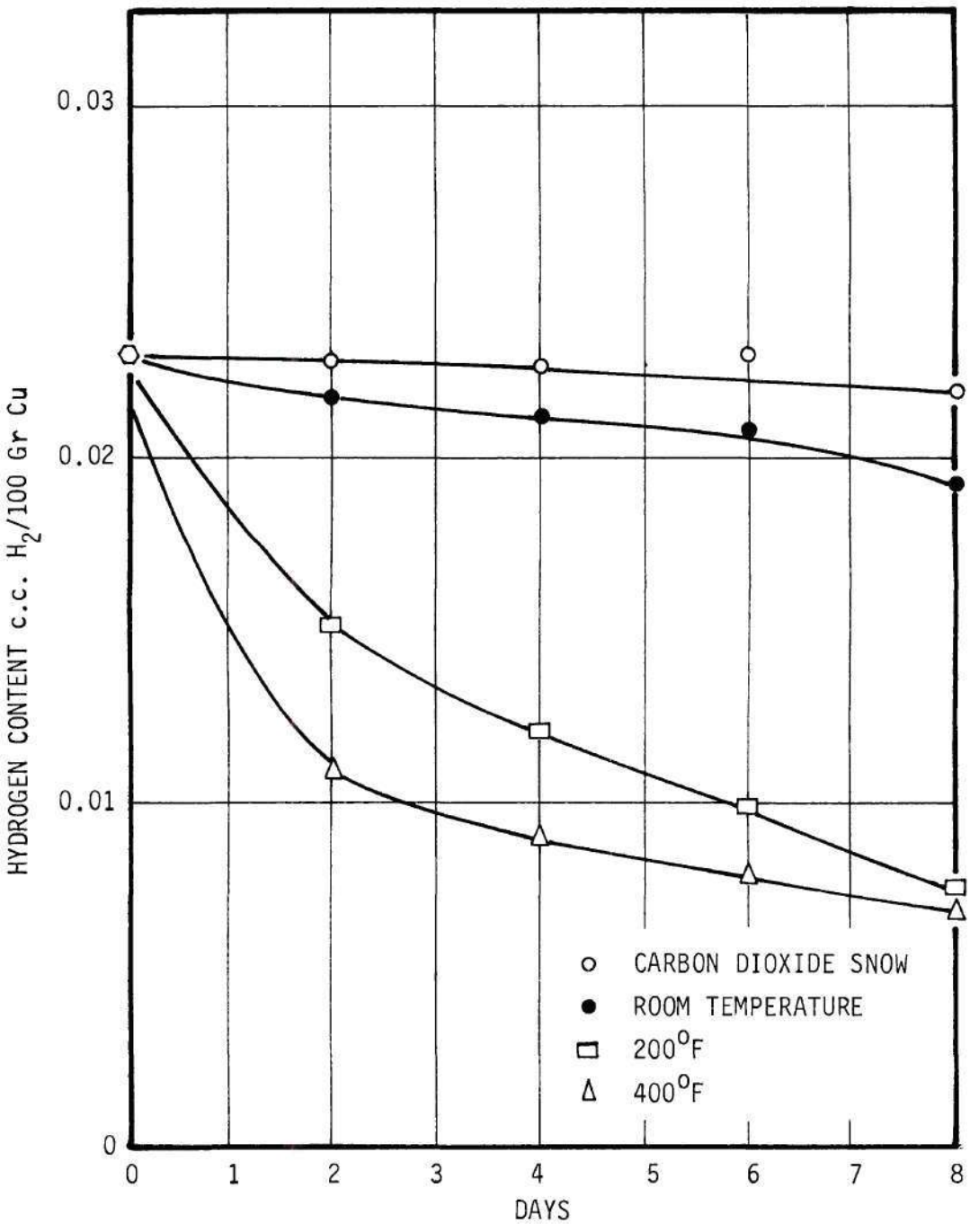


Figure 14. Isotherms of the Hydrogen Content Vs. Time for Four Sets of Samples.

should be performed to disclose degree of homogeneity varying with the depth of the bath, as seen in Figure 15.

In order to study and determine the composition of the furnace atmosphere in contact with the metal during the process, an Orsat gas analysis should be made of this gas obtaining percentages of oxygen, carbon monoxide, carbon dioxide and moisture. Such an analysis should be performed several times during the poling operation.

Errors incurred by the handling of the sampling device and the type of device used will have a bearing on the results obtained both in the oxygen and hydrogen content in the copper due to material of sampler, exposure to atmosphere, time for sampling, cooling during sampling, and solidification rate.

Cooling velocity of the sample in the mold has a great effect on the determination of the oxygen in copper if this is done using the photomicrograph comparison method. This can be controlled by the mold material which could be copper or graphite. Figure 16 shows two structures of copper containing the same amount of oxygen but solidified in two different ways. Figure 16(A) shows a photomicrograph of a sample which was cooled very slowly in a preheated graphite mold. A very large dendritic structure is evident. By contrast, Figure 16(B) shows copper which was solidified at a fast rate in a cold graphite mold; a very small dendritic growth resulted. Both photomicrographs were etched with 50 percent nitric acid and photographed at 75 X magnification. A graphite mold will reduce oxides at the surface in contact with the graphite. In order to avoid an erroneous determination of the amount of copper oxide eutectic, readings should be ideally taken from the center of the sample,but in any case,

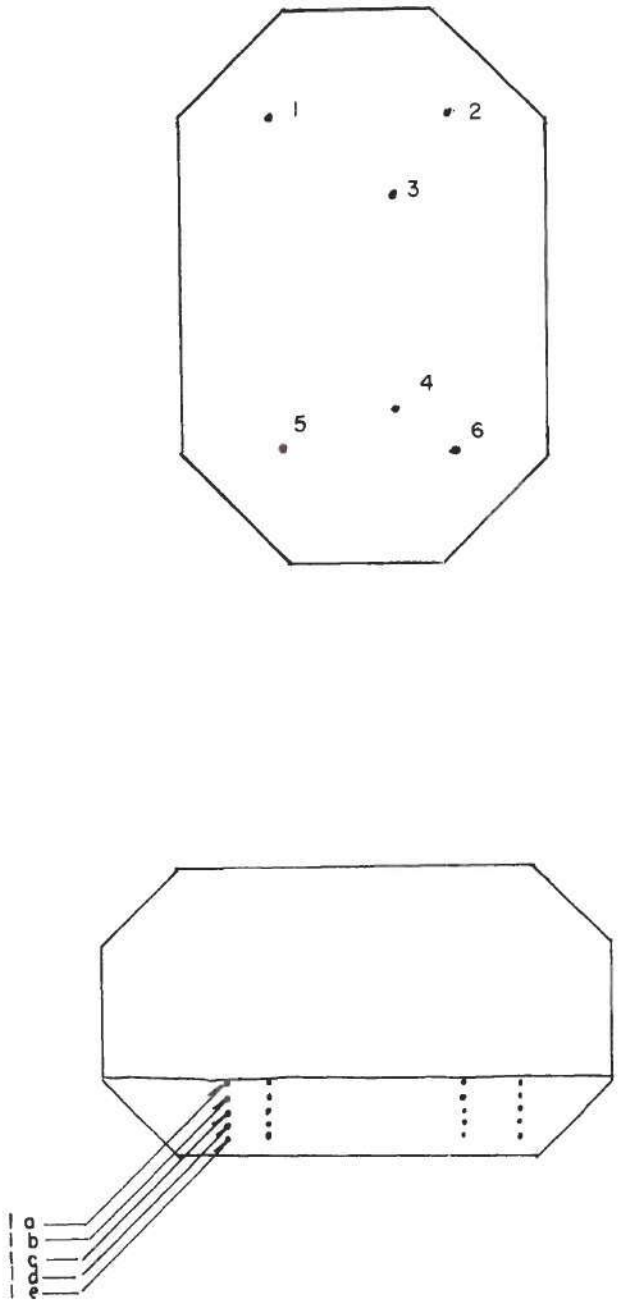
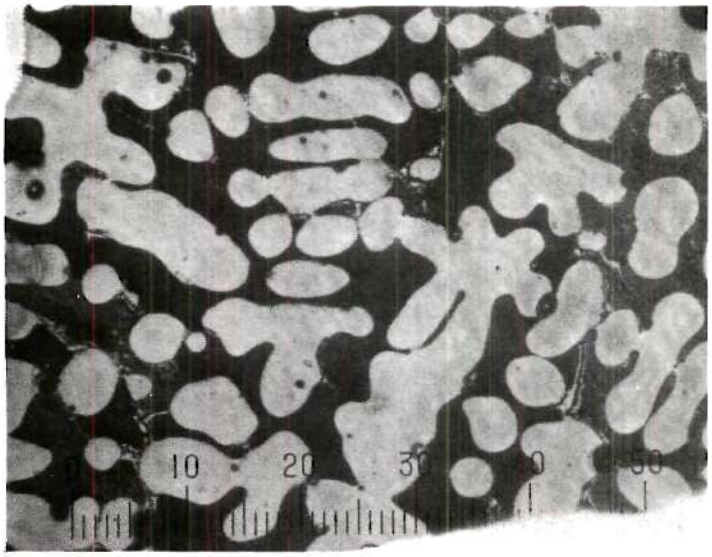
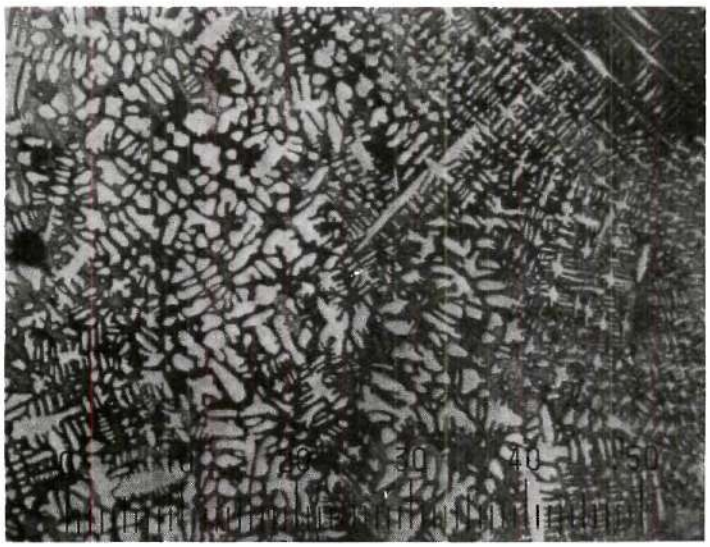


Figure 15. Schematic Diagram Showing Location of Samples in the Copper Furnace.



(a) SLOW COOLING 0.303% O_2 BY H_2 REDUCTION
0.346% O_2 BY VACUUM FUSION



(b) FAST COOLING 0.256% O_2 BY H_2 REDUCTION
0.343% O_2 BY VACUUM FUSION

Figure 16. Photomicrographs of Copper Showing Difference in Dendritic Growth Due to Cooling Velocity Mag. 75X.

sampling closer than 0.25-inches from the surface of the sample should be avoided.

Care must be taken to prevent a diffusion of the gas in solution in the copper while solidification takes place. It is known that at high temperatures gases diffuse extremely fast. If too much time elapses between taking of the sample until final solidification, the sample will show a lesser gas content in solution.

CHAPTER VI

DETERMINATION OF OXYGEN IN COPPER

Oxygen in copper can be determined by microprobe analysis, X-ray fluorescence, hydrogen reduction, and by metallographic examination; the last two methods were used for this experiment and will be described below.

Hydrogen Reduction

Oxygen content in copper for this set of experiments was determined by hydrogen reduction which consisted of placing a fifteen-gram sample in a quartz or a porcelain boat and heating it under hydrogen atmosphere. This setup is depicted in Figure 17.

The sample to be tested was first submerged in a solution of nitric acid (20 percent) to remove the surface oxide. It was then dried with acetone, and then weighed to a precision of one thousandth of a gram. Next the sample was placed in a boat made of quartz or porcelain, which was placed in a porcelain tube. Before the tube was placed in a furnace at a temperature of 900^{o}C for two hours, it was sealed on both ends with rubber stoppers and dry hydrogen gas was passed through it for ten minutes. The dry hydrogen was obtained by passing hydrogen gas through drying agents of anhydrous calcium chloride and phosphorus pentoxide.

If sulphur was determined, the gas from the tube was led through an absorber bottle containing a definite volume of a cadmium chloride (3 percent) solution for absorption of the sulphur hydride. The sulphur

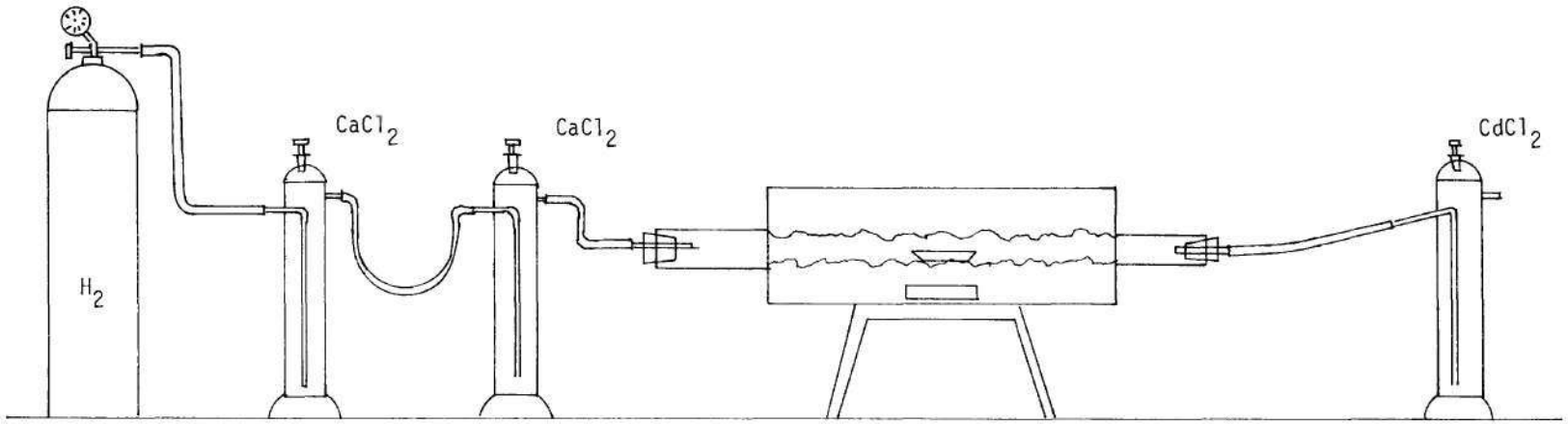


Figure 17. Schematic Diagram Showing Setup of Apparatus for Determining Oxygen by the Hydrogen-Reduction Method.

solution was then titrated against a standard iodine solution.

The dry hydrogen passing over the copper sample must maintain a constant flow rate through the entire experiment. The most desirable flow rate is two bubbles per second. This was checked by the flow of gas through the cadmium chloride solution at the end of the porcelain tube. The hydrogen must flow at this rate for two hours, and then for thirty minutes while the sample cools in the porcelain tube out of the hot zone at the furnace.

The most critical procedure in the process is the accurate weighing that must be made on the copper sample before and after the oxygen has been removed. Calculation of percent of oxygen can be made by the following formula:

$$\text{Percent } O_2 = \frac{\text{Original weight of sample-weight of sample after heating}}{\text{Original weight of sample}} \times 100$$

Metallographic Method

The amount of oxygen present in cast copper can be calculated by estimating the percentage of cuprous oxide eutectic present in the structure. The cuprous oxide eutectic forms a network throughout the structure which in a photomicrograph appears dark, while the pure copper crystals appear "brick red." The use of a polarized light improves the color contrast of the copper oxide in the copper matrix. The area covered by the cuprous oxide network is directly proportional to the oxide content of the copper. An optical comparison of the structure with a set of standard photomicrographs, which have been calibrated by the hydrogen reduction method, is a common practice in the copper industry. Some disagreement exists among the major copper producers concerning the oxygen

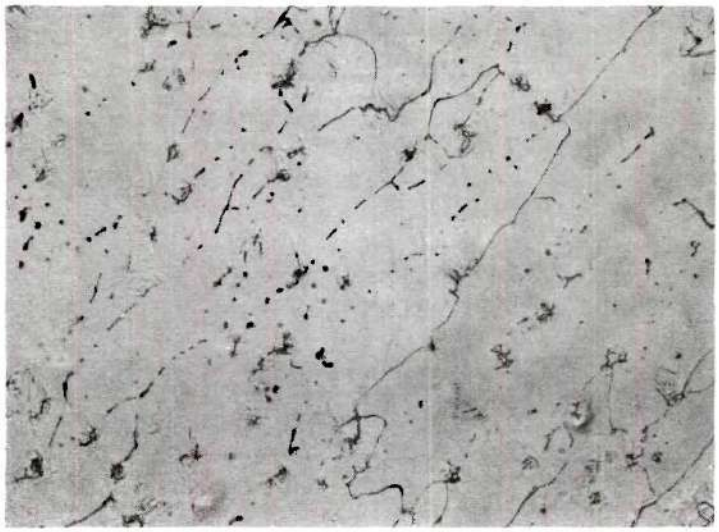
content that corresponds to the eutectic structure. A set of photomicrographs accurately calibrated by this author using the hydrogen reduction method mentioned above is included below. These structures were photographed with a magnification of 75 X.

The copper samples were cut, ground, polished, and etched using the electropolisher Disa-Electopol. The processing details are tabulated below.

Etching Solution D-2 = 250 ml. Phosphoric acid
500 ml. Water
250 ml. Ethyl alcohol
50 ml. Propanol
5 gr. Urea

Polishing Operation = 20 Seconds
4.75 amperes per square centimeter

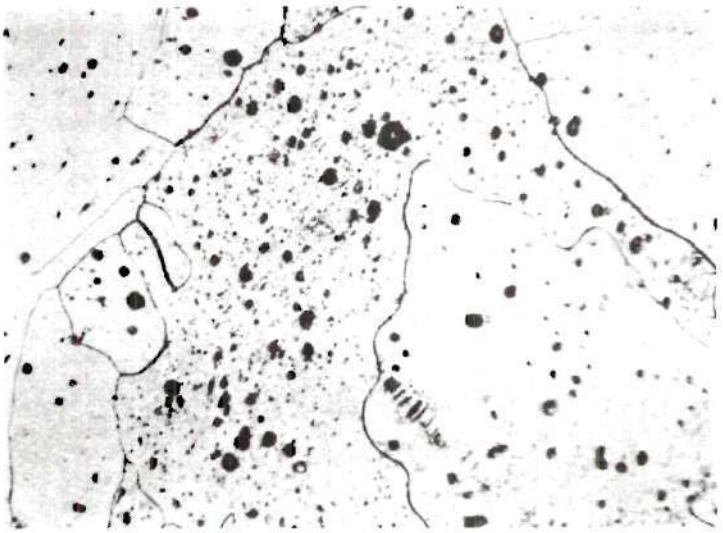
Etching Operation = 9 Seconds
1.25 amperes per square centimeter



D - 2 ELECTROPOLISHED x75
(a) 0.02% O_2

D - 2 ELECTROPOLISHED x75
(b) 0.03% O_2

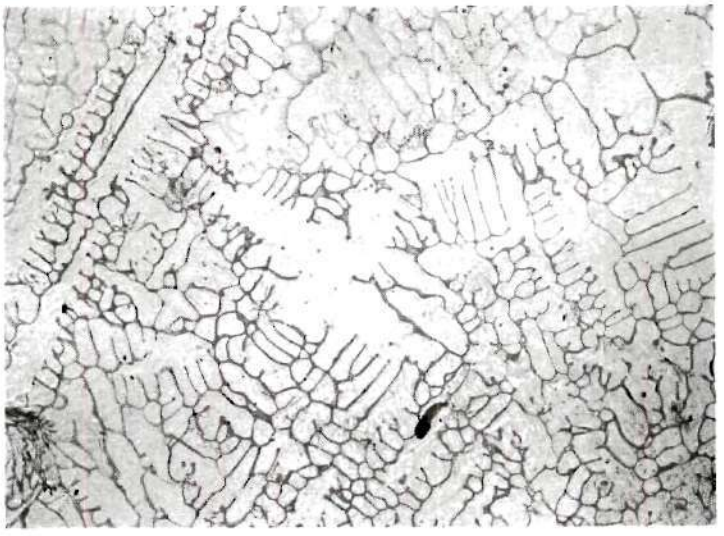
Figure 18. Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.



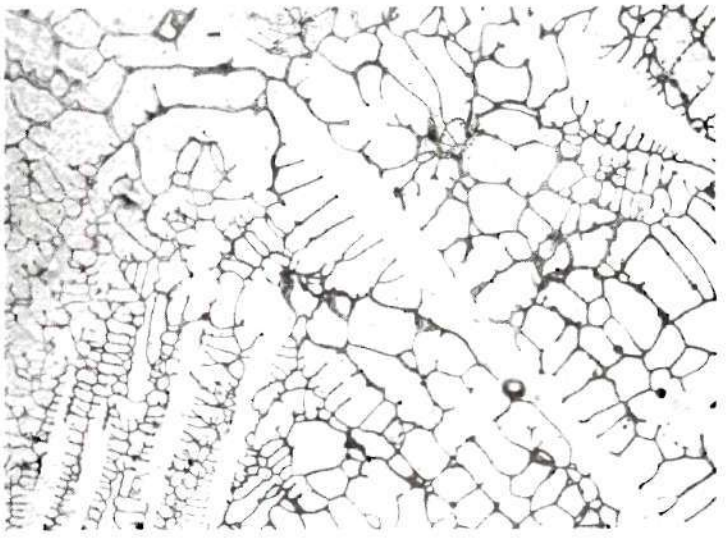
(c) 0.04% O_2 x75

(d) 0.05% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

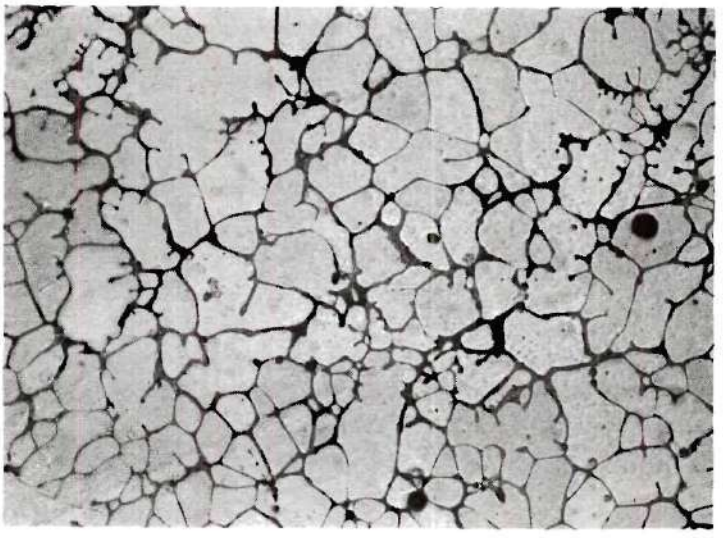


(e) 0.055% O_2 x75

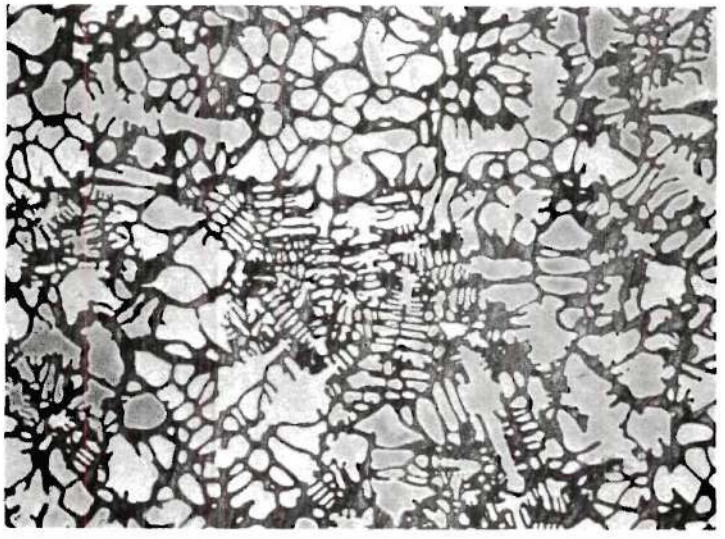


(f) 0.062% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

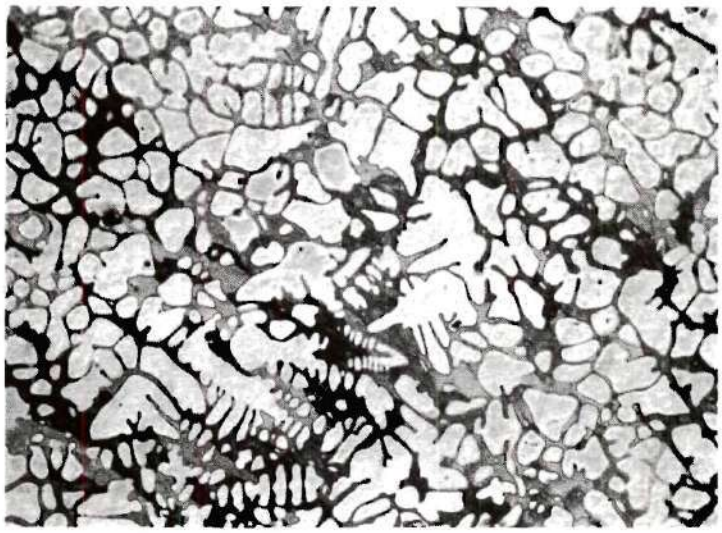


(g) 0.075% O_2 x75

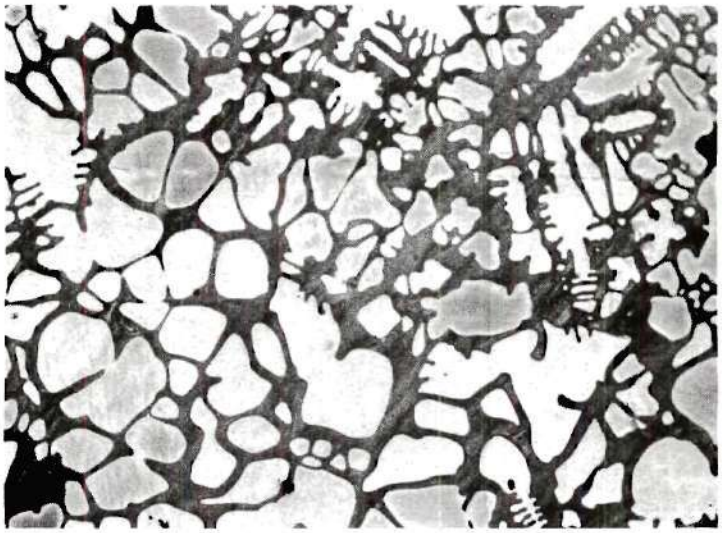


(h) 0.095% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

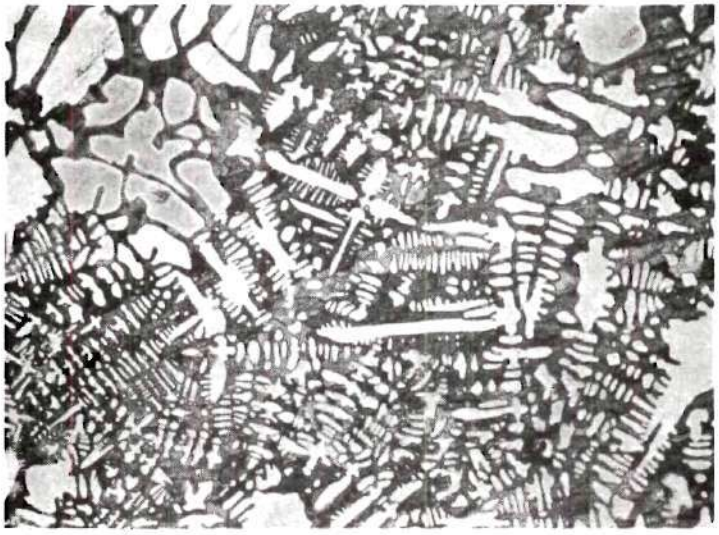


(i) 0.12% O_2 x75

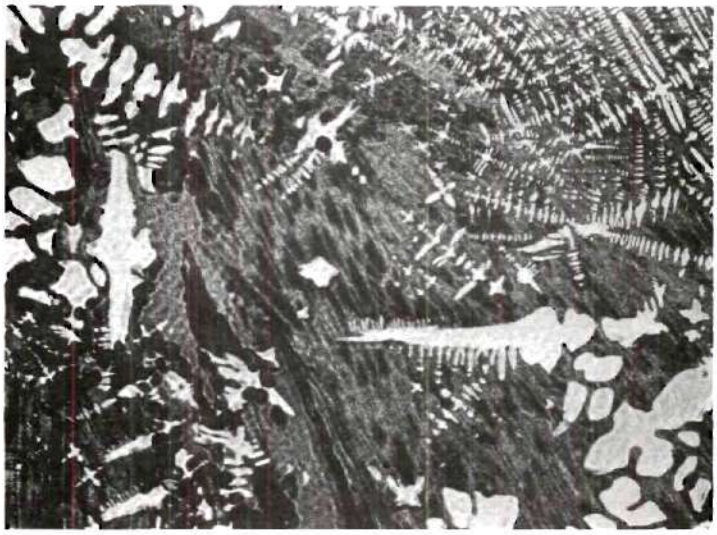


(j) 0.20% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

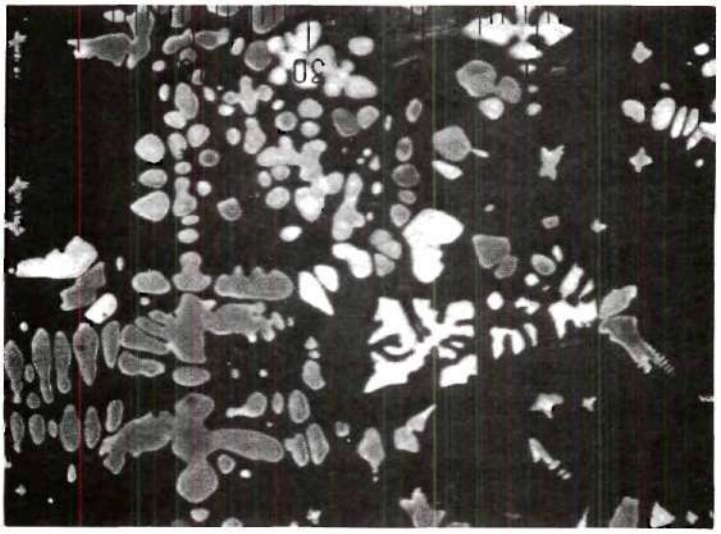


(k) 0.25% O_2 x75

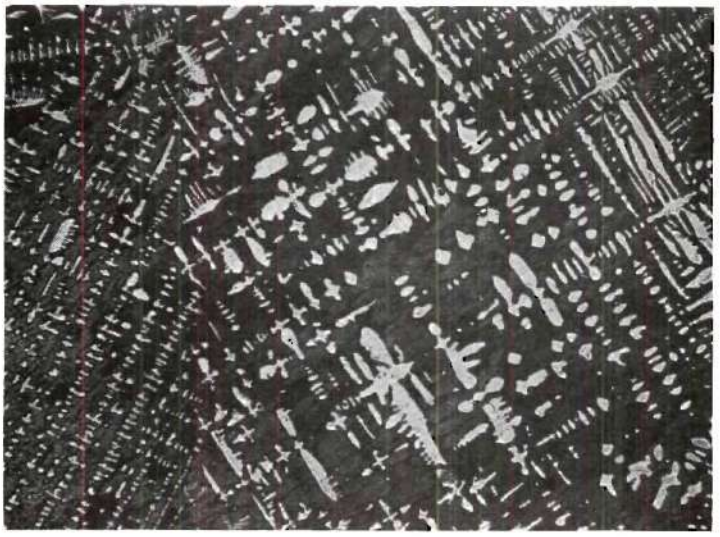


(l) 0.30% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

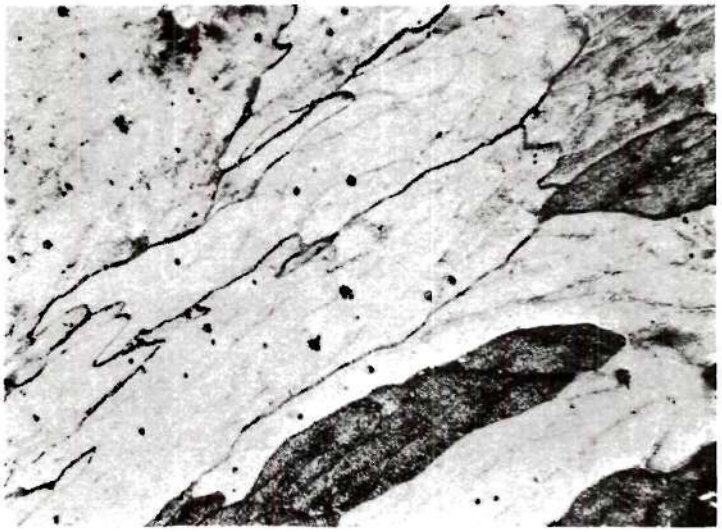


(m) 0.34% O_2 x75

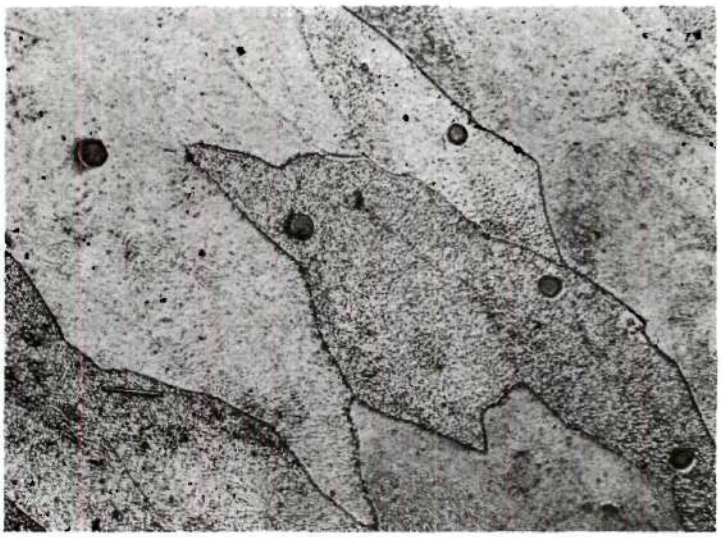


(n) 0.37% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

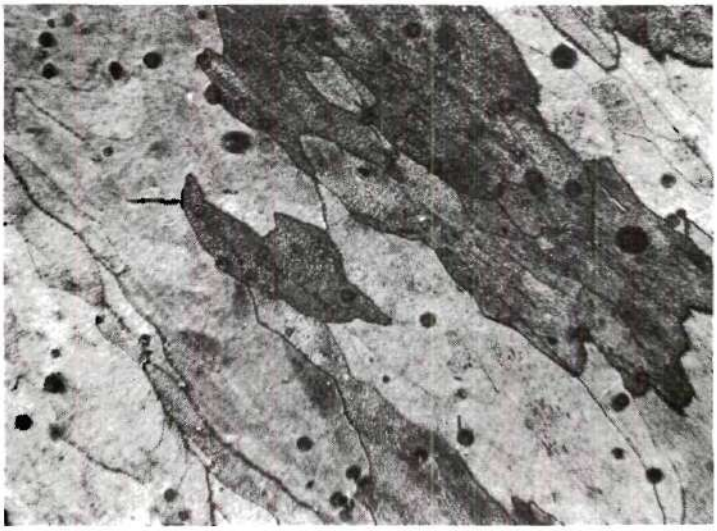


(o) 0.41% O_2 x75

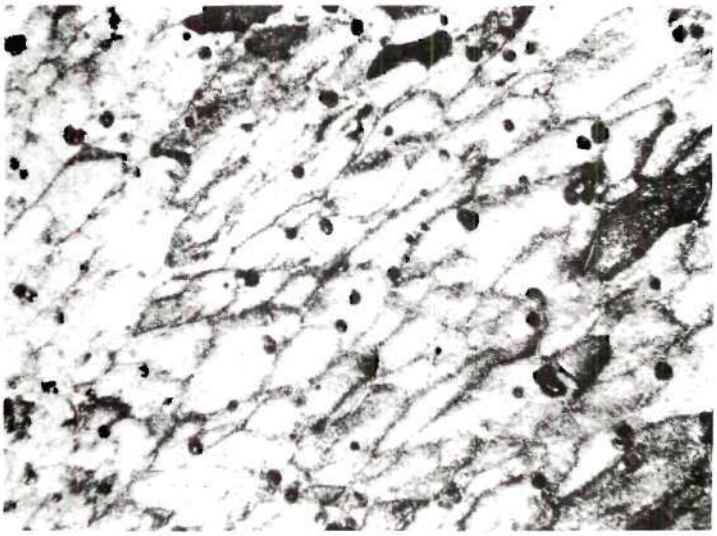


(p) 0.45% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

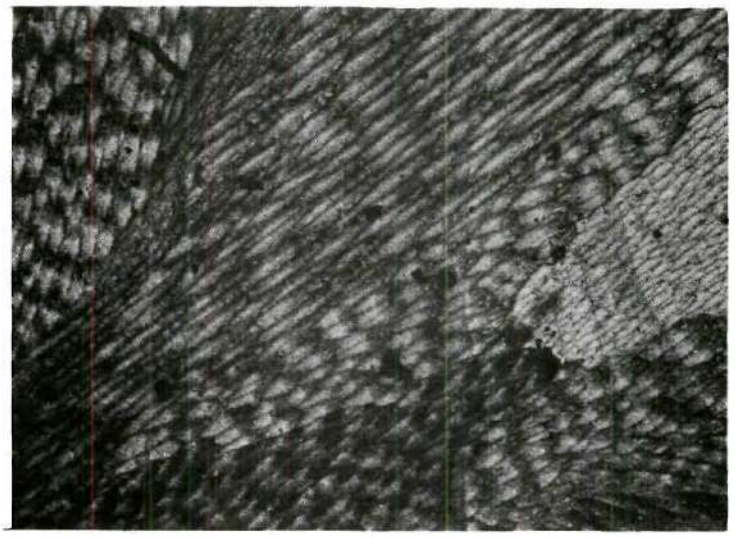


(q) 0.49% O_2 x75

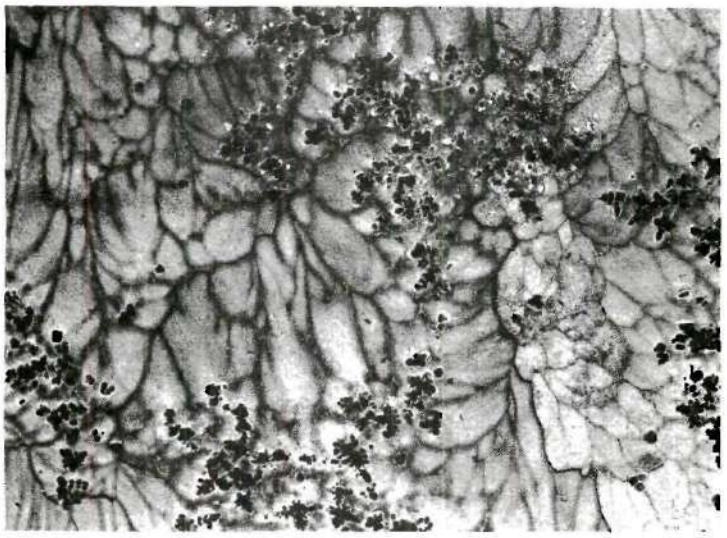


(r) 0.55% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

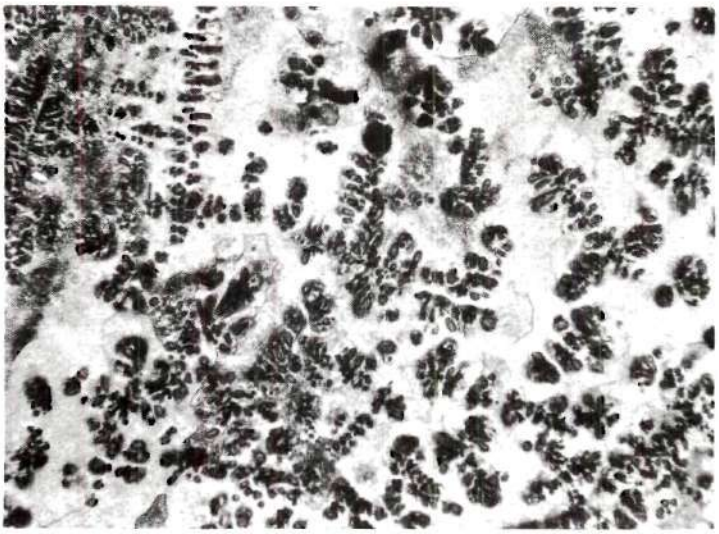


(s) 0.60% O_2 x75

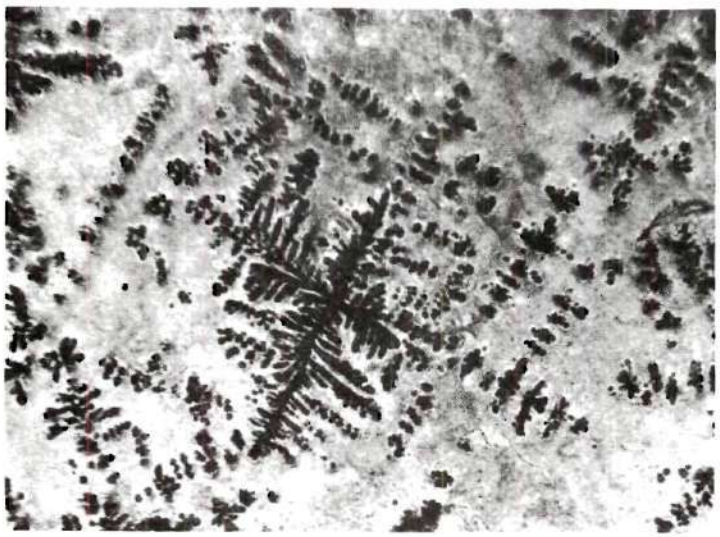


(t) 0.72% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.



(u) 0.83% O_2 x75



(v) 0.91% O_2 x75

Figure 18. (Continued) Set of Photomicrographs Showing Different Oxygen Contents Calibrated by Hydrogen Reduction Method.

CHAPTER VII

HYDROGEN AND TOTAL GAS ANALYSIS

Description of Apparatus

The apparatus used for the gas analysis shown in Figure 19 consists of a heating chamber (A) made of quartz glass with its lower portions covered with asbestos paper. The chamber contains a quartz crucible, 1-$\frac{1}{2}$ inches long by 7/8 inches inside diameter, where the copper sample is placed. The mercury lift (B) is used as a manometer to indicate that a good vacuum has been obtained at the left side of the main valve (C). This valve connects the heating chamber with the rest of the apparatus.

D_1, D_2, and D_3 are absorbers which contain phosphorus pentoxide (P_2O_5), pure magnesium (Mg) chips, and calcium oxide (CaO), respectively. These absorbers eliminate water vapor, oxygen, and sulphur dioxide from the gas stream. The hydrogen filter (E) consists of a palladium silver alloy tube with a closed end. In order to keep the hydrogen filter at 500°F (which is the temperature for best diffusion of hydrogen) a heating coil (F) of nichrome wire is wound on the outside of the tube and controlled by a powerstat. (G) is a cold trap to prevent mercury vapors from getting on the apparatus. The three-stage mercury diffusion pump (H) has a two-fold purpose in this set-up. It provides a vacuum of approximately 10^{-6} torr and pumps the gases through the entire apparatus.

(I) represents the Toepler-McLeod gauge calibrated in cubic centi-

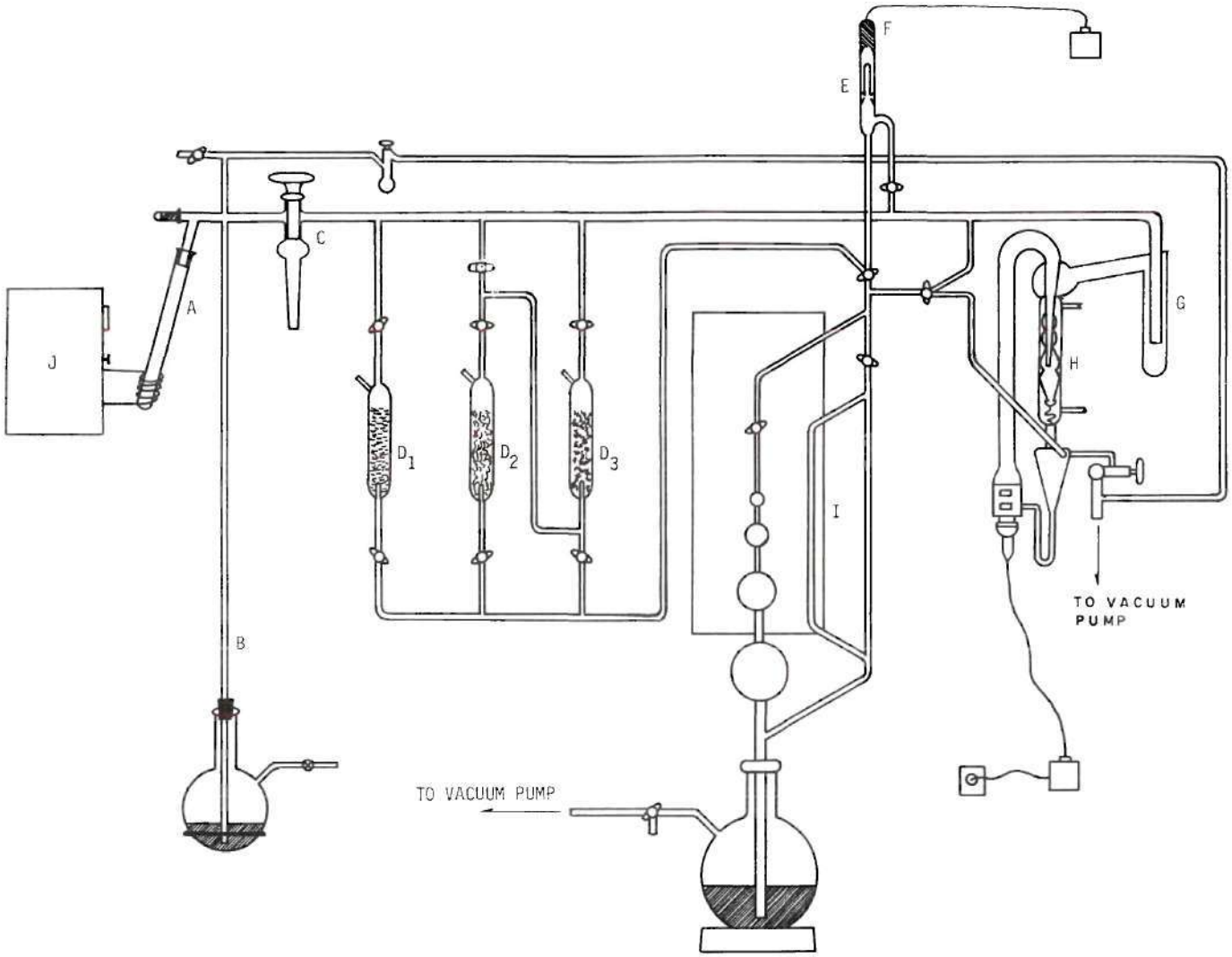


Figure 19. Schematic Diagram Showing Apparatus Used for Gas Analysis.

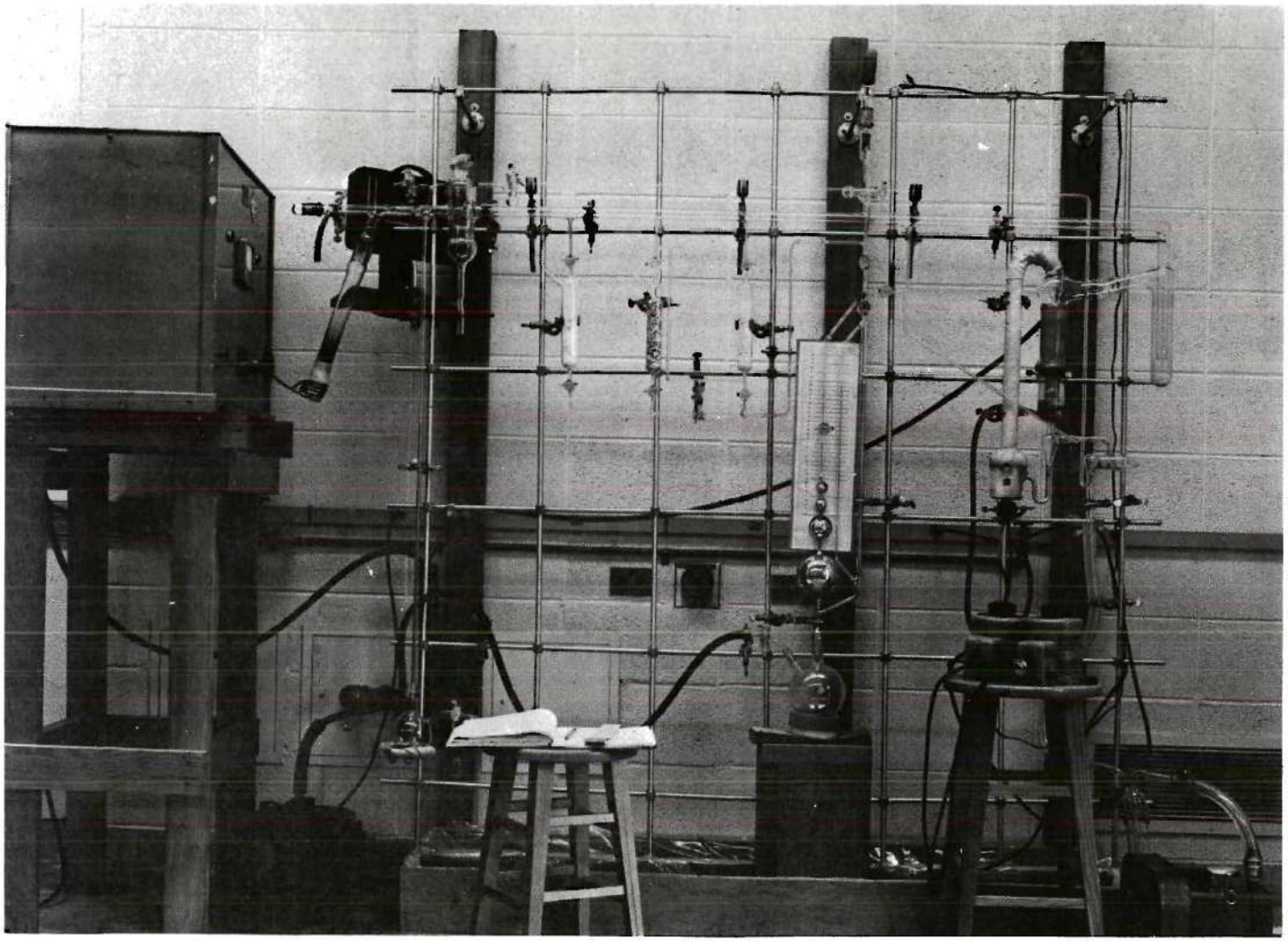


Figure 20. Apparatus Used for the Determination of Hydrogen in Copper.

meters. This gauge measures the amount of gases and then flushes them out to continue their circulation through the different absorbers. A vacuum pump is used to force the mercury back into its container once the determination has been accomplished.

(J) is a Lepel high-frequency induction furnace.

Calibration of McLeod-Toepler Gauge

In order to measure the amount of gases present in the copper sample, a volumetric calibration of the McLeod gauge was necessary. This was accomplished by making marks at different levels of the McLeod (Figure 21) and filling the gauge up to each mark with mercury and weighing it to an accuracy of one thousandth of a gram. After filling the gauge to the desired mark, the mercury was degassed in order to remove any air bubbles which had formed. The filling operation was done by using a fine capillary funnel two feet long and a vacuum pump. The capillary was introduced to the bottom of the gauge and mercury was poured through it.

The results obtained in the calibration are shown below.

Volume obtained from stopcock to:

First Mark = 0.1227 cubic centimeters

Second Mark = 0.2330 cubic centimeters

Third Mark = 0.6056 cubic centimeters

Fourth Mark = 3.2829 cubic centimeters

Fifth Mark = 12.9404 cubic centimeters

Sixth Mark = 63.9843 cubic centimeters

Total volume of McLeod gauge = 543.882 cubic centimeters.

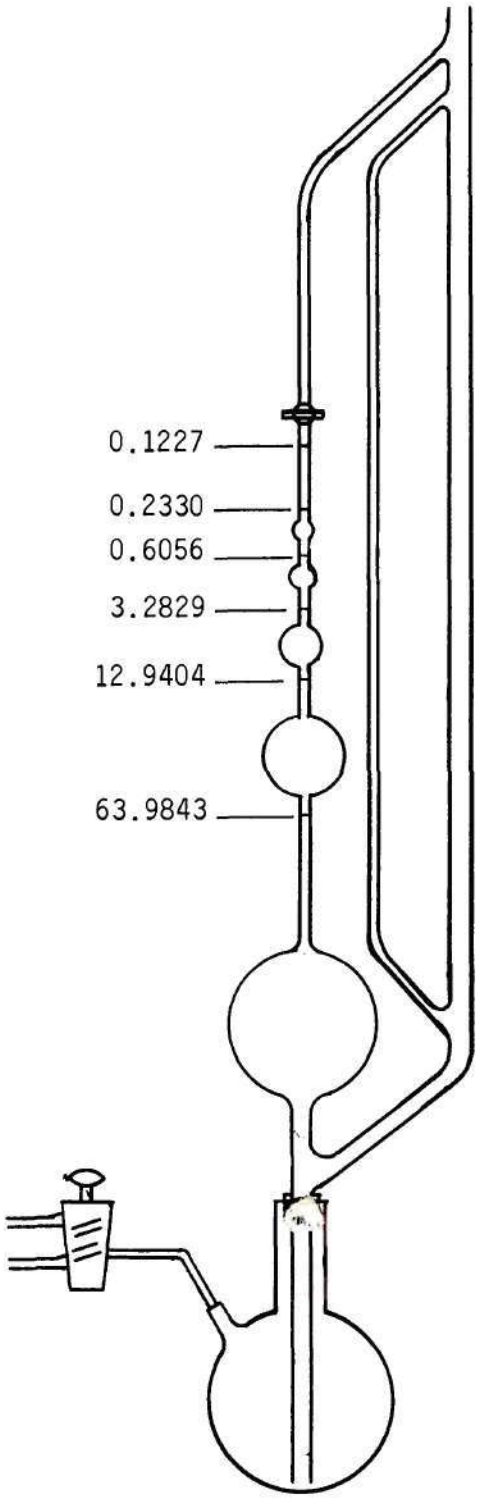


Figure 21. Toepler - McLeod Gauge.

Testing for Vacuum

A vacuum of at least 10^{-5} torr was necessary to perform the hydrogen determination in copper. Some difficulty was encountered with the leakage of air through some of the stopcocks of the system. After obtaining a good vacuum, the system was sealed by closing the main valve to the vacuum pump. Pressure was measured in the system after two, four, and twelve hours with the system isolated from the pump. An initial pressure increase was measured though a Tesla-ionization leak detector did not indicate any pin-hole leaks.

In the next procedure the apparatus was divided into three sections and each section was tested for vacuum tightness individually. It was found that one of the valves going to the Toepler-McLeod gauge was not sufficiently tight. Using new vacuum grease and working the stopcock into the opening solved this problem. A vacuum of at least 10^{-5} torr was subsequently obtained without difficulty. This low pressure was achieved in thirty-five minutes after the pumping was started. Degassing of the chemicals contained in the absorbers was performed by heating them to $350^{\circ}F$ with a degassing gun while continuously pumping the system. This operation was carried out every eight or ten analyses to insure good vacuum condition inside the gas absorbers.

Operating Procedure

The copper specimens to be analyzed must be filed in order to eliminate the surface oxide and then cleaned in ethyl alcohol, dried, and weighed accurately to within one thousandth of a gram. Carbon dioxide snow was used for storing the samples when it was not possible to perform

the analysis immediately after casting.

For this investigation, samples were charged in the apparatus one at a time. The apparatus was designed so that up to three samples could be placed in the slots shown in Figure 22. Each sample was dropped one at a time by using a magnetic device and a piece of steel. This method can save time because it is unnecessary to interrupt the vacuum. All determinations performed in this work were done individually.

The specimen was placed inside a quartz crucible 1-$\frac{1}{2}$ inches long by 7/8-inch inside diameter. A vacuum of 10^{-6} torr was achieved throughout the entire system. Care was taken to be sure that all absorption bulbs were carefully degassed and that no gases were left in any part of the system. All valves leading to the absorbers and to the palladium diffusion tube were closed and only the path leading to the McLeod gauge was open.

The sample was then heated and melted by a high frequency furnace which delivered 10 kilocycles per second at a maximum power of 2.5 kw. Gases evolving from the specimens were driven through the entire free path to the end of the Toepler-McLeod gauge where they were collected and measured. It was found that the mercury diffusion pump would not handle or circulate gases if their volumes exceeded 2.5 cm^3. Therefore, the maximum allowable weight of the copper sample was 8 grams. For most analyses, the sample was approximately 4 grams.

The gases were collected in the McLeod gauge, shown in Figure 21. Their volumes were measured and then they were flushed to the absorber containing phosphorous pentoxide, where the water vapor was removed. During the hot extraction period, measurements were made at five-minute

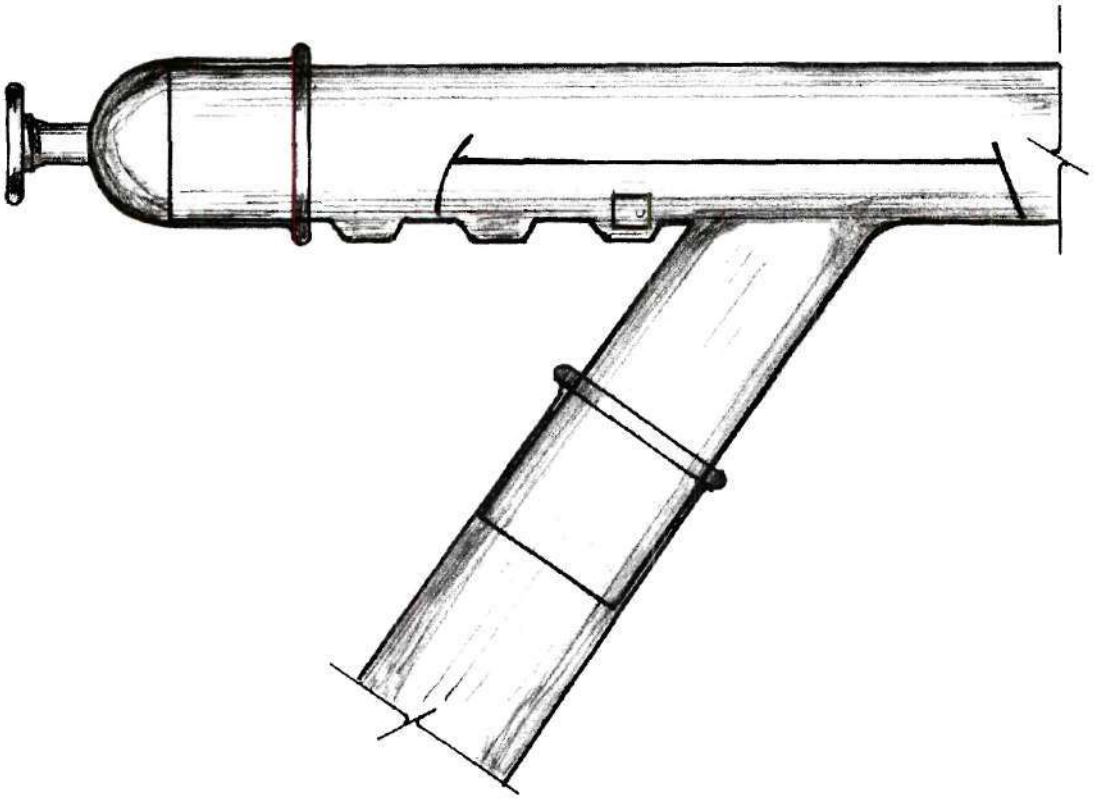


Figure 22. Sample Holding Chamber of the Gas Analysis Apparatus.

intervals until the evolution of the gas had practically ceased or until the difference between the two columns of the McLeod gauge was 0.1 cm or less. After each measurement the gas was transferred to the absorption container using the McLeod as a Toepler pump. This step evacuated the system and all the gases contained in the P_2O_5 chamber were ready to be circulated and measured again.

Oxygen can be analyzed in this apparatus. However, the oxygen determinations given in this paper were obtained by the hydrogen reduction method which proved to be of greater accuracy.

The sample circulation and measurement of the gases described above was used for each of the absorbers, concluding by measuring the amount of hydrogen present in the total gas. This was done by passing the dried gas through a palladium-silver diffusion tube which was allowing only the hydrogen to pass through it. This tube, shown in Figure 23, was kept at a temperature of 500°F to facilitate diffusion.

In order to insure the complete diffusion of hydrogen, measurements were performed every ten minutes until a negligible amount of hydrogen was measured. After this point a final measurement was done after thirty more minutes.

Example of Hydrogen Determination

The analysis was started at 2:05 p.m. and the sample melted at 2:11 p.m. While this took place, the main valve was kept open. At 2:16 p.m. (5 minutes after melting) the main valve was closed and the amount of gas was measured; it showed 0.321 c.c.

At 2:27 p.m. the volume was 0.272 c.c.

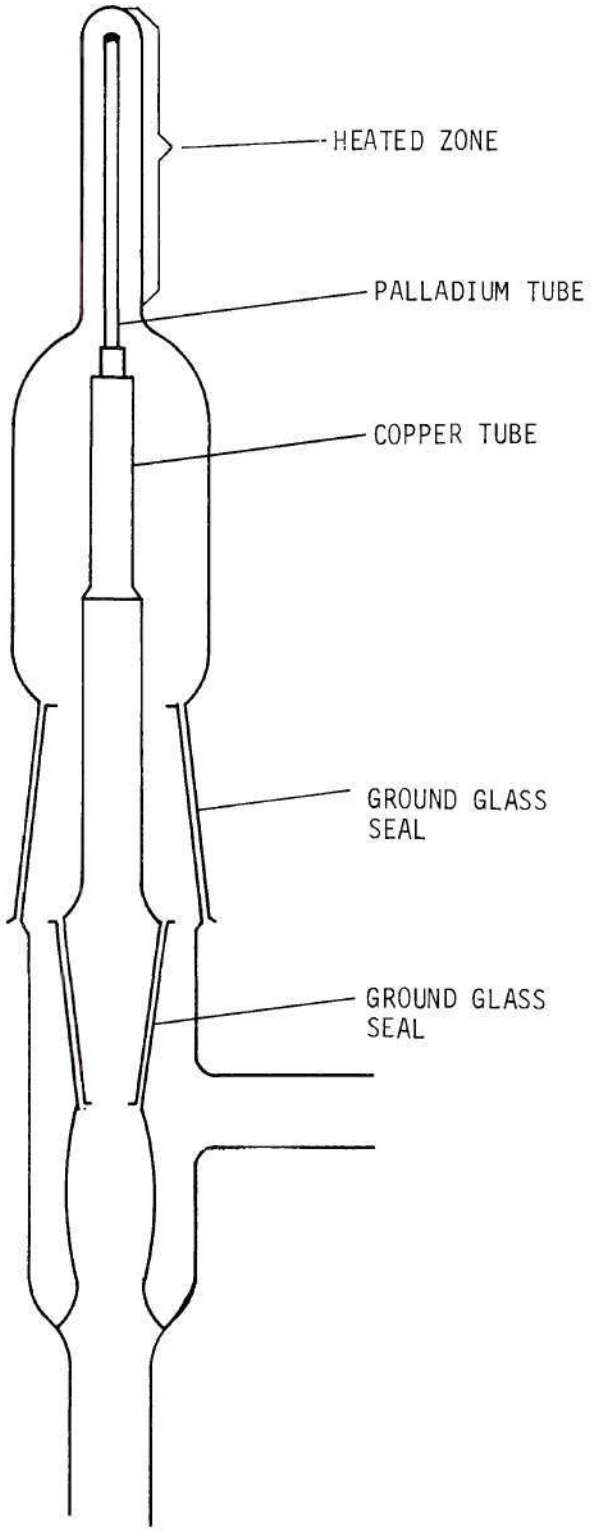


Figure 23. Palladium Tube for the Diffusion of Hydrogen.

At 2:38 p.m. the volume was 0.107 c.c.

At 2:50 p.m. the volume was 0.0092 c.c.

At 3:03 p.m. the volume was 0.00062 c.c.

At this point the main valve was opened as the mercury went down. A new measurement at 3:07 p.m. was taken and the volume was 0.163 c.c.

At 3:12 p.m. the valve was closed.

At 3:19 p.m. the volume was 0.083 c.c.

At 3:30 p.m. the volume was 0.0089 c.c.

At 3:41 p.m. the volume was 0.00040 c.c.

The main valve was then opened again and a new determination was taken. The valve was left open.

At 3:52 p.m. the volume was 0.063 c.c.

At 4:03 p.m. the volume was 0.0057 c.c.

At 4:15 p.m. the volume was 0.0008 c.c.

At 4:27 p.m. the volume was 0.0001 c.c.

At 4:40 p.m. no reading was possible.

CHAPTER VIII

RESULTS AND DISCUSSIONS

The previously described method for analyzing gases in copper was used to investigate the variation of the gas content over several runs of commercial copper refining by poling. A similar pattern for the different runs was observed.

During three different refining cycles, samples were taken every ten minutes with a ladle and poured into a copper mold to chill-solidify them. The samples were immediately placed in carbon dioxide snow after solidification and stored there until analyzed. The hydrogen content and total gas content were determined by the hot vacuum extraction method and the oxygen content by the hydrogen reduction method.

The results are summarized in Tables 9, 10, and 11 and plotted below. The hydrogen content, with minor exceptions, increases steadily during each poling cycle. The oxygen content decreases until a value of 0.03 percent oxygen is reached, thus ending the poling cycle.

A large amount of moisture was also extracted from the copper samples. This moisture content was included in the total gas content which increases from 1-2 cc./100 g. to 4-12 cc./100 g. during the cycle. The total gas content includes other gases which were not analyzed. The total gas content therefore must be greater than the sum of the hydrogen and the oxygen contents. The first sample of cycle number three, however, yielded a lower total gas content than the sum of the hydrogen and oxygen

Table 9. Hydrogen, Oxygen and Total Gas Content of Copper Samples Taken Every Ten Minutes During the Poling Operation No. 1

	H_2(c.c/100 g.)	O_2(%)	Total Gas (c.c/100 g.)
10 min.	0.23	0.39	1.50
20 min.	----	----	----
30 min.	0.151	0.368	1.55
40 min.	1.00	0.34	4.06
50 min.	----	0.346	4.34
60 min.	1.19	----	5.85
70 min.	1.35	0.308	5.68
80 min.	2.25	0.032	12.54

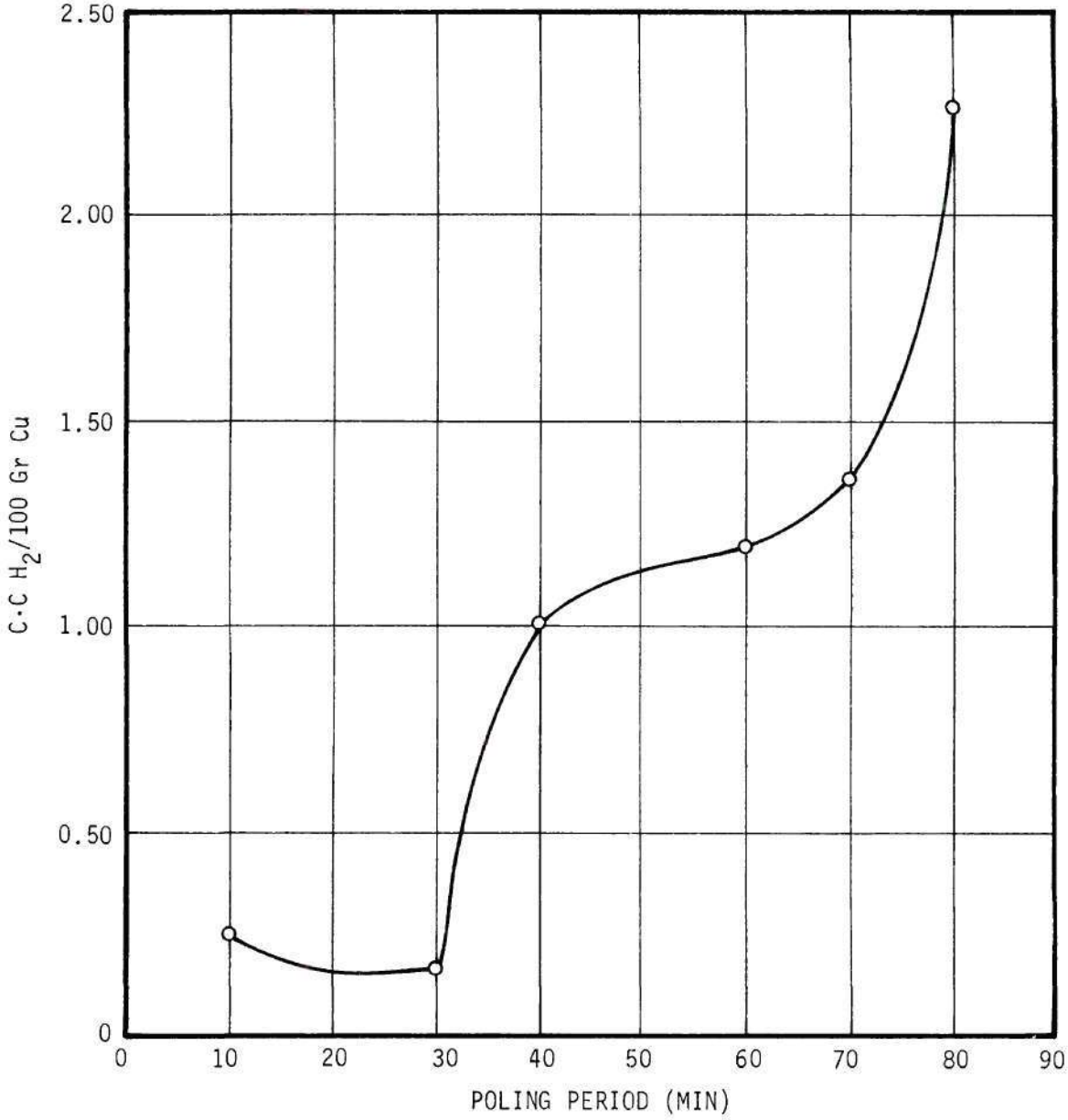


Figure 24. Hydrogen Content Vs. Time During Poling No. 1.

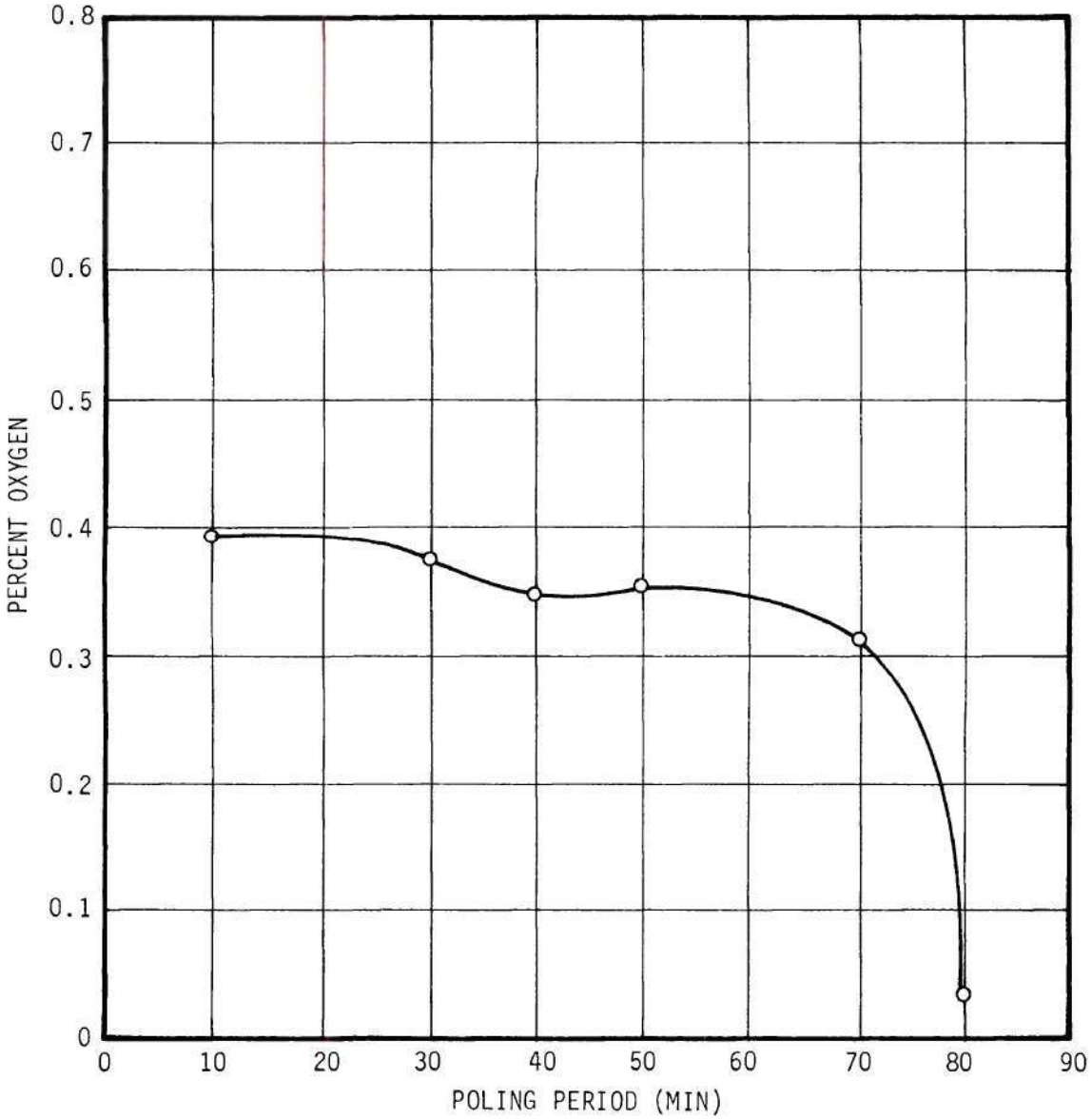


Figure 25. Oxygen Content Vs. Time During Poling No. 1.

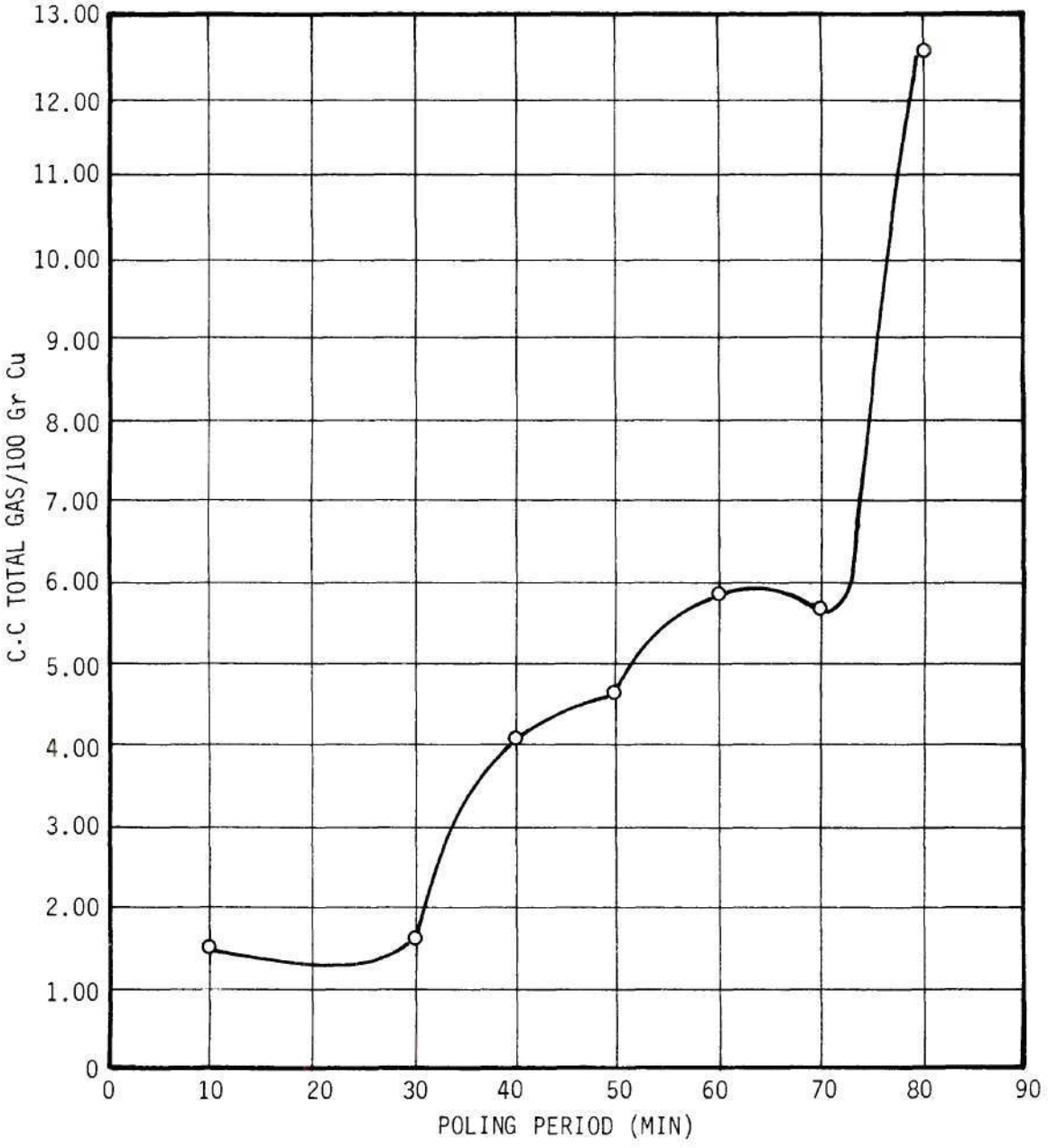


Figure 26. Total Gas Content Vs. Time During Poling No. 1.

contents. This can probably be accounted for by the fact that the oxygen analysis was done on a different sample, of the same run, from the one used for the hydrogen analysis.

Discussion of Results

The main purpose of the poling process is to reduce the cuprous oxide present in the oxygen-purified copper. This process is slow at the beginning while the pole is liberating steam. As the cycle continues, the pole becomes charcoal which will reduce the cuprous oxide. This stage is indicated by a rapid decrease in the oxygen content from above 0.3 percent to below 0.1 percent.

The hydrogen content starts low, then rises to around one cubic centimeter per one hundred grams of copper. It remains there for twenty to thirty minutes and then increases thereafter. Poling cycle number three does not show the plateau. This can be attributed to the short length of the cycle.

The water formation reaction is controlled by the mass law as expressed in Equation (7)

$$K_1 \cdot X = (C_{H_2})^2 \cdot (C_O) \quad .$$

After a few minutes poling, the copper is exposed to steam (X) at a pressure of one atmosphere. Thereby, the hydrogen content adjusts itself to approximately 1.0 cubic centimeter per one hundred grams and the oxygen content to slightly over 0.35 percent. This condition is obtained after sixty minutes of poling in cycle number one, as shown in Figures 24, 25, and 26. Cycles two and three reach this condition after thirty minutes

Table 10. Hydrogen, Oxygen and Total Gas Content of Copper Samples Taken Every Ten Minutes During the Poling Operation No. 2

	H_2(c.c/100 g.)	O_2(%)	Total Gas (c.c/100 g.)
10 min.	0.19	0.875	2.87
20 min.	0.916	0.652	3.21
30 min.	0.781	0.40	3.45
40 min.	1.024	0.115	5.22
50 min.	1.382	0.0745	7.68
60 min.	2.326	0.0350	8.71
70 min.	2.433	0.0354	9.37
80 min.	2.328	0.051	9.67

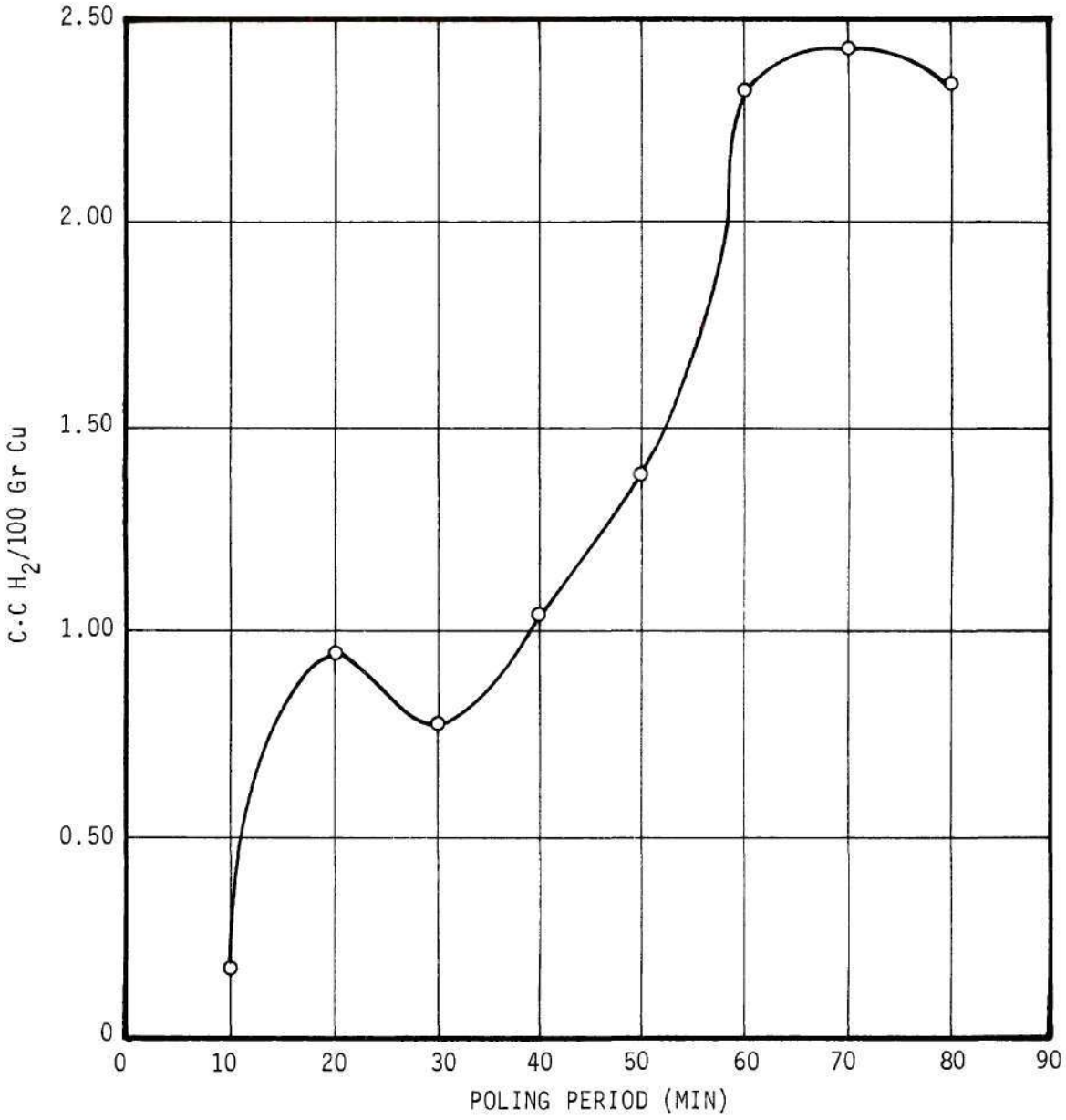


Figure 27. Hydrogen Content Vs. Time During Poling No. 2.

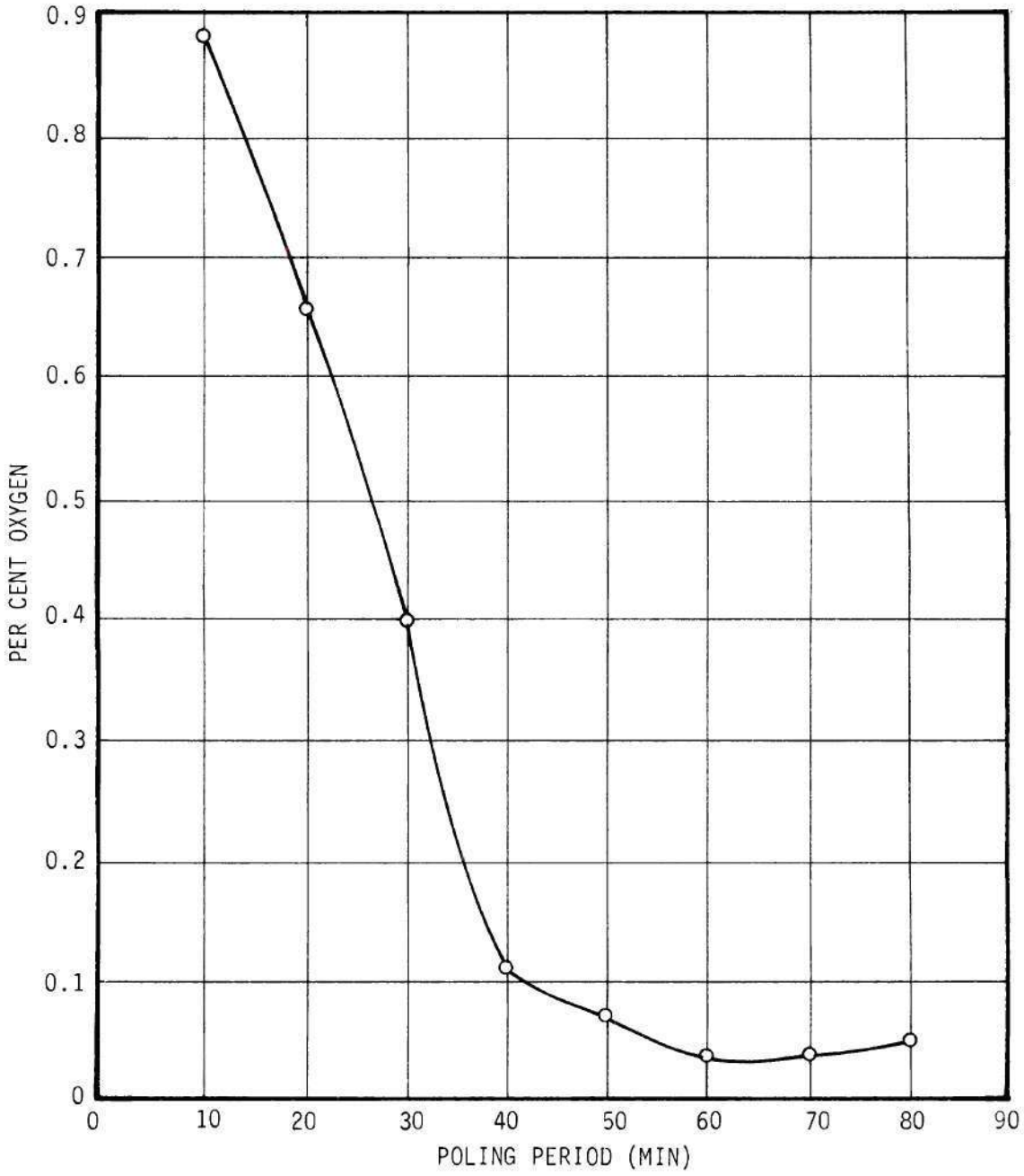


Figure 28. Oxygen Content Vs. Time During Poling No. 2.

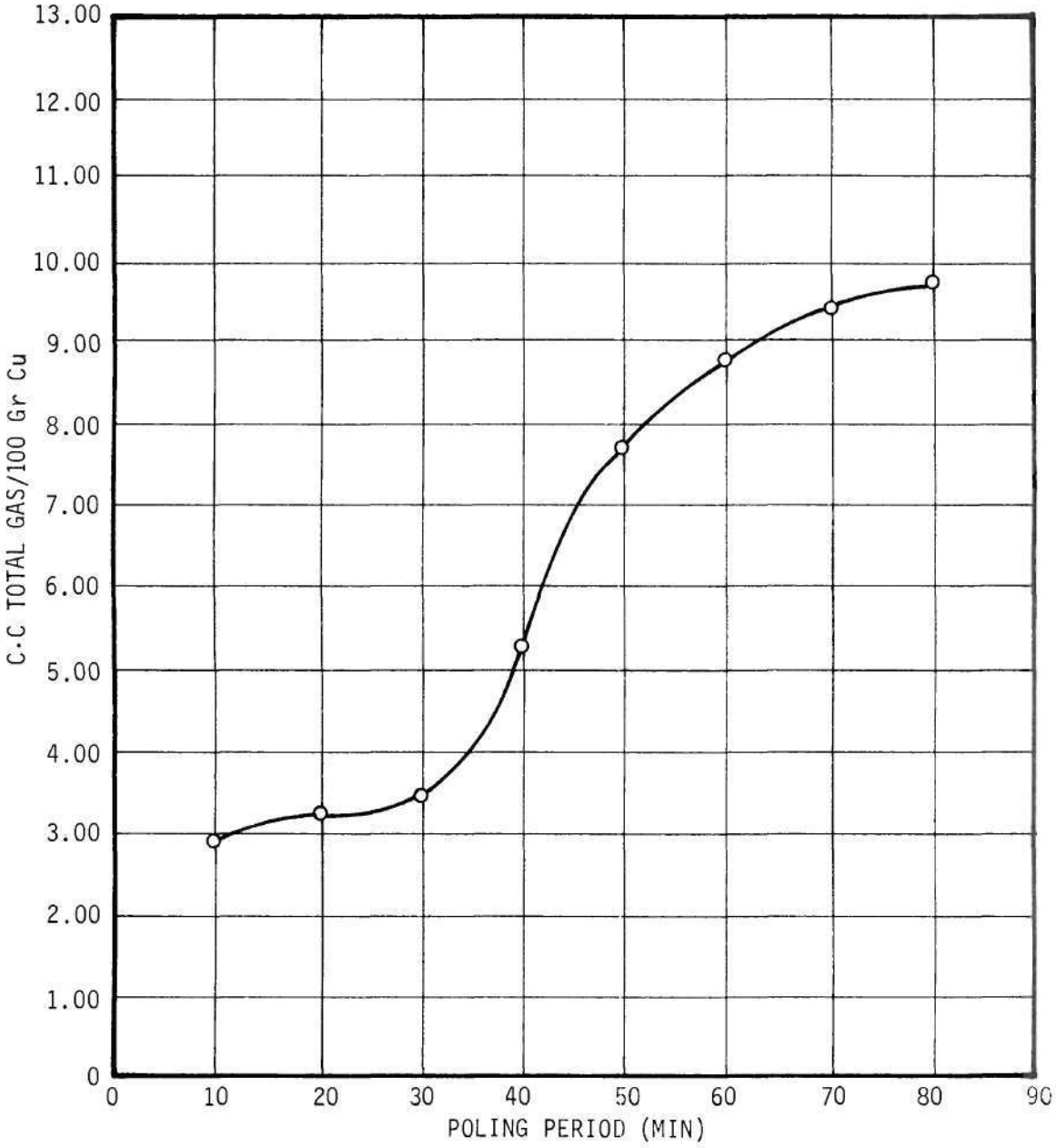


Figure 29. Total Gas Content Vs. Time During Poling No. 2.

Table 11. Hydrogen, Oxygen and Total Gas Content of Copper Samples Taken Every Ten Minutes During the Poling Operation No. 3

	H_2(c.c/100 g.)	O_2(%)	Total Gas (c.c/100 g.)
10 min.	0.216	0.815	0.86
20 min.	0.413	0.390	1.74
30 min.	0.865	0.329	1.78
40 min.	1.434	0.09	2.21
50 min.	1.832	0.033	4.03
60 min.	1.879	0.031	4.68

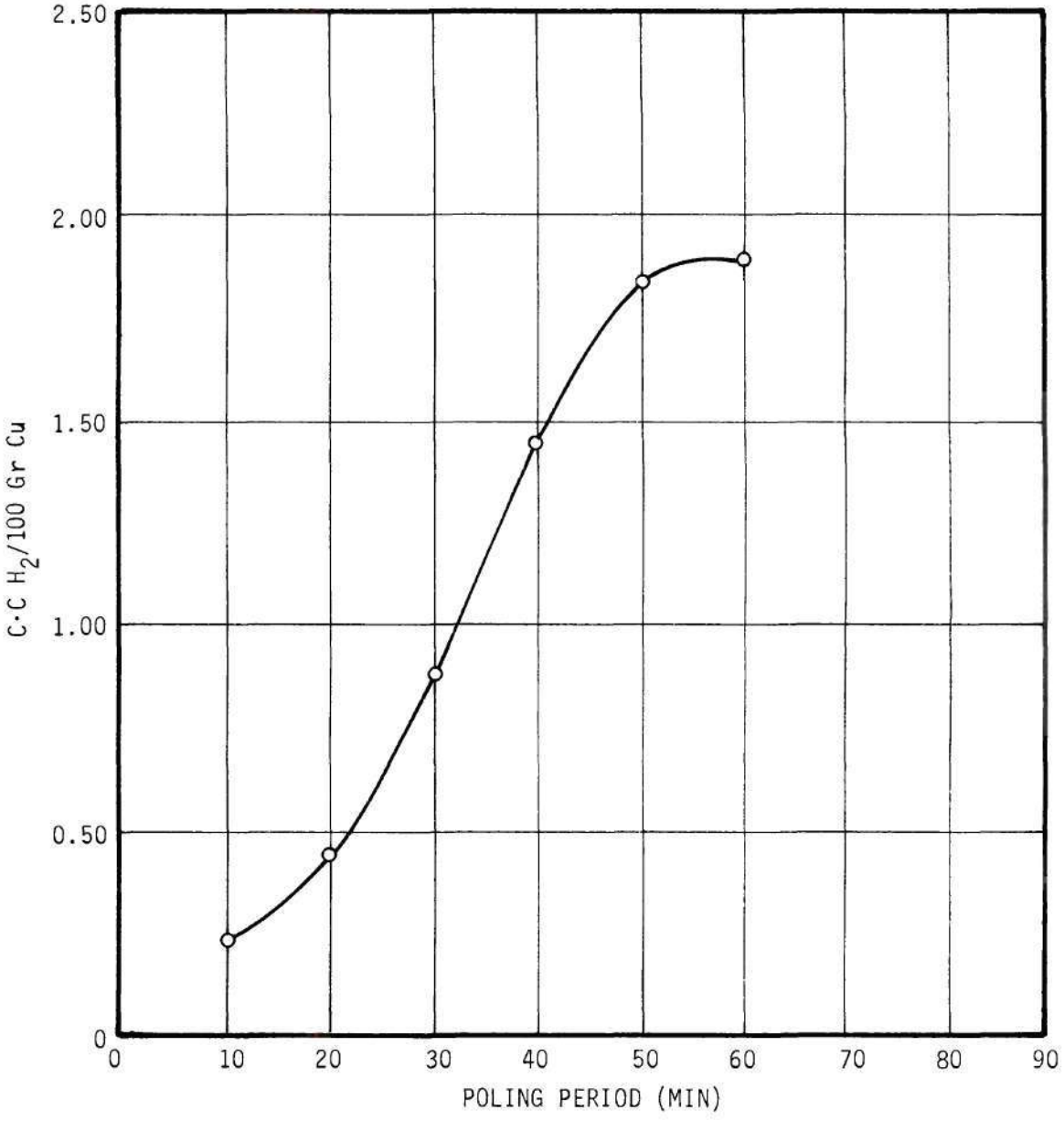


Figure 30. Hydrogen Content Vs. Time During Poling No. 3.

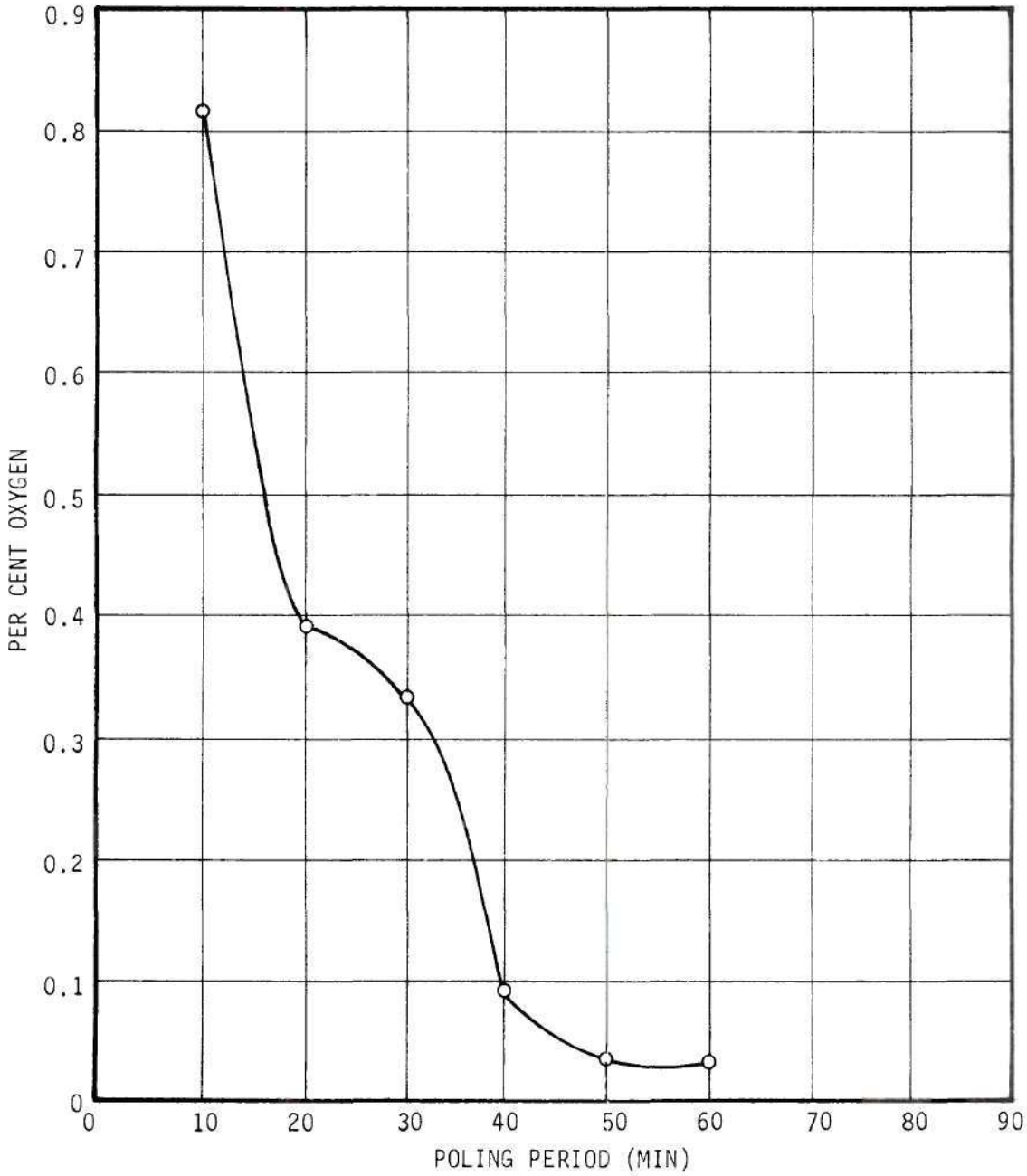


Figure 31. Oxygen Content Vs. Time During Poling No. 3.

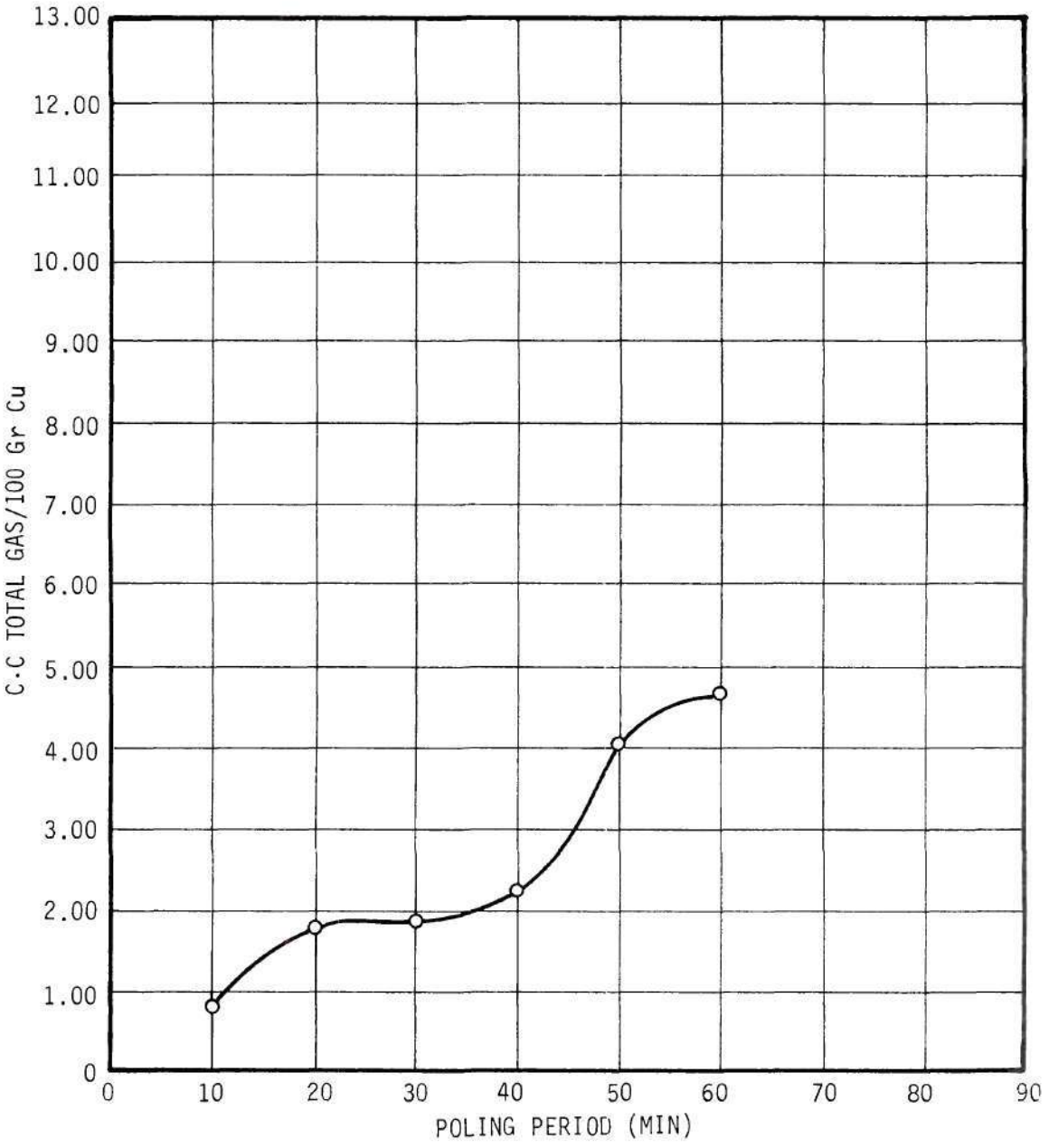


Figure 32. Total Gas Content Vs. Time During Poling No. 3.

Table 12. Concentration of Hydrogen and Oxygen and Constant $K_1 \cdot X$ Obtained from Samples Taken at Ten Minute Intervals During Poling No. 1

Time (min.)	C_{H_2}	C_{O_2}	$K_1 \cdot X$
10	0.022	0.39	1.885×10^{-4}
20			
30	0.015	0.365	0.82×10^{-4}
40			
50		0.34	0.34
60			
70	1.35	0.30	0.547
80	2.3	0.03	0.149

Table 13. Concentration of Hydrogen and Oxygen and Constant $K_1 \cdot X$ Obtained from Samples Taken at Ten Minute Intervals During Poling No. 2

Time (min.)	C_{H_2}	C_{O_2}	$K_1 \cdot X$
10	0.18	0.875	0.0284
20	0.92	0.655	0.555
30	0.781	0.40	0.244
40	1.024	0.115	0.120
50	1.382	0.07	0.134
60	2.326	0.035	0.189
70	2.433	0.035	0.207
80	2.328	0.05	0.272

Table 14. Concentration of Hydrogen and Oxygen and Constant $K_1 \cdot X$ Obtained from Samples Taken at Ten Minute Intervals During Poling No. 3

Time (min.)	C_{H_2}	C_{O_2}	$K_1 \cdot X$
10	0.216	0.815	0.038
20	0.413	0.39	0.068
30	0.865	0.33	0.247
40	1.434	0.09	0.185
50	1.832	0.033	0.111
60	1.879	0.03	0.106

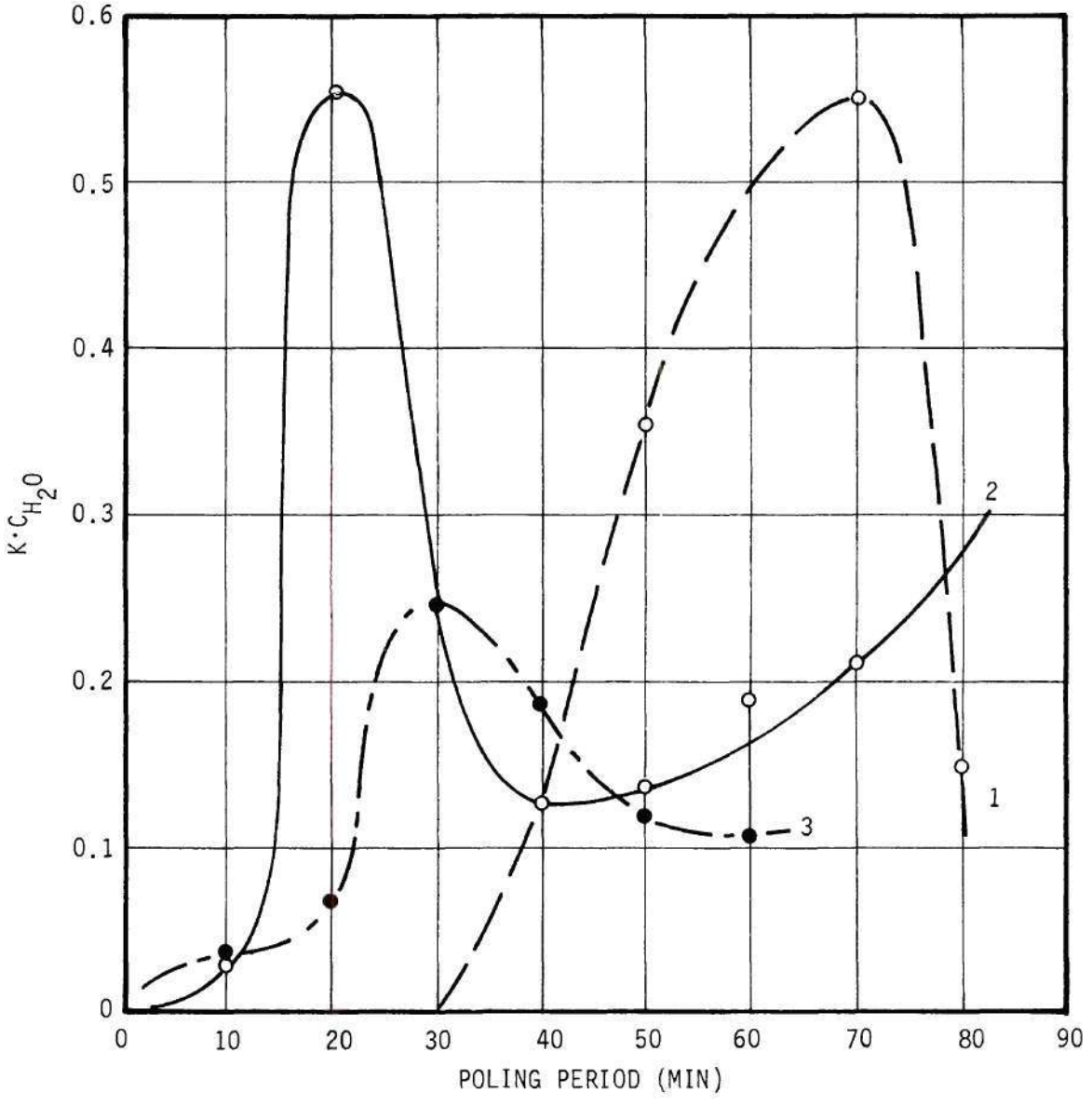


Figure 33. Equilibrium Constant $K_1 \cdot X$ Vs. Time for the Three Poling Operations.

of poling, as shown in Figures 27, 28 and 29, for cycle number two and Figures 30 and 31 for cycle number three.

Before reaching saturation, the product of oxygen and hydrogen and hydrogen concentrations will be less than the equilibrium value. The X value, obtained from Equation (7), is lower than the saturation value, shown in Figure 33, for the beginning of each cycle.

Each poling cycle was characterized by an early stage where the metal is exposed to steam at a pressure of one atmosphere. During this early period an equilibrium condition between the metal and steam was reached. Thus, the $K_1 \cdot X$ value increased to a maximum of 0.55, as seen in Figure 33.

Once this equilibrium had been reached, the pole was dried and the steam concentration decreased. Simultaneously, the charcoal exerted a powerful reducing action on the oxygen in the metal. For the above two reasons, the product $K_1 \cdot X$ must decrease. It falls to just above one-tenth for the three cycles.

If poling is continued beyond this point the low oxygen content obtained will permit a heavy pickup of hydrogen. This is demonstrated by the curves exhibiting hydrogen content versus time, as seen in Figures 24, 27, and 30. If the poling is continued beyond this point, the $K_1 \cdot X$ value will increase again due to an increasing hydrogen content and an essentially constant oxygen content. This is seen in Figures 27, 28, and 33. Differences in position and height of the curves may be observed in Figure 33. These differences were probably caused by the non-uniformity in size and weight of the hardwood poles used for the poling.

Suggestions for Further Work

More runs should be made with known poling conditions, such as weight of the poles, moisture content, type of hardwood, and diameter of poles. Also, to avoid the unfavorable effect of steam, poling with dried charcoal should be tried.

CHAPTER IX

RECOMMENDATIONS

The unfavorable effects of the gases unavoidably dissolved in poled copper may be eliminated by a thorough degassing process. This degassing may either be performed in batches or in continuous processing.

Three batch degassing methods used in the steel industry may be applicable in the treatment of copper metal.

Figure 34 depicts degassing the metal in the ladle. This process involves placing a ladle of copper in a vacuum chamber to pump off the unwanted gaseous content. This method will not degass the metal at the bottom of the ladle. This difficulty can be eliminated by applying an induction coil around the ladle. As the metal is stirred by induction, all the metal will eventually be exposed to the vacuum action at the surface of the metal.

Stream degassing, as illustrated in Figure 35, shows how the metal is treated by this method, which works as follows.

An empty ladle is placed in a vacuum chamber and a second ladle is filled with molten metal and sealed to the top of the vacuum chamber. A stopper is then removed and the copper is allowed to pour into the bottom ladle. This exposes the copper as it falls through the vacuum. Because of short exposure times this system could be used primarily to reduce hydrogen content.

Figure 36 illustrates another possible degassing method. This con-

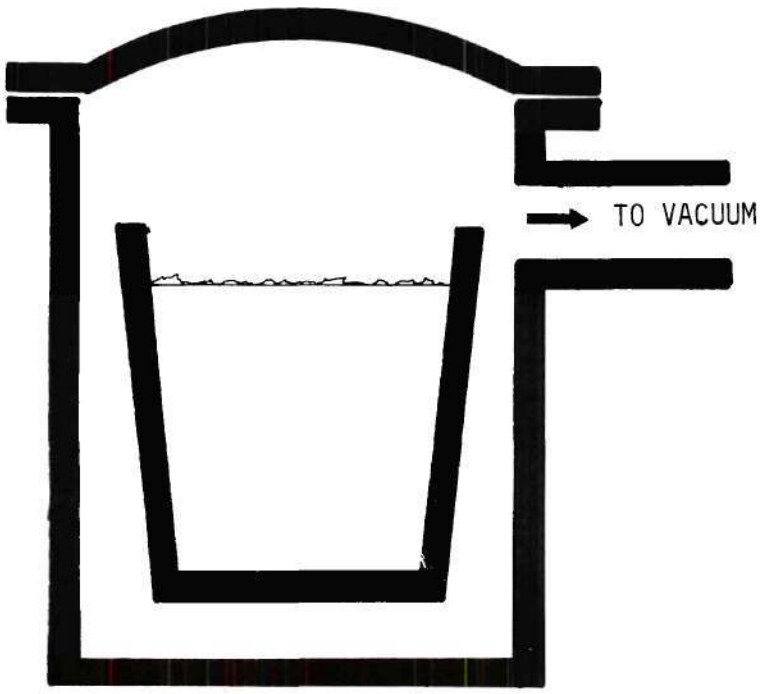


Figure 34. Metal Degassing in Ladle.

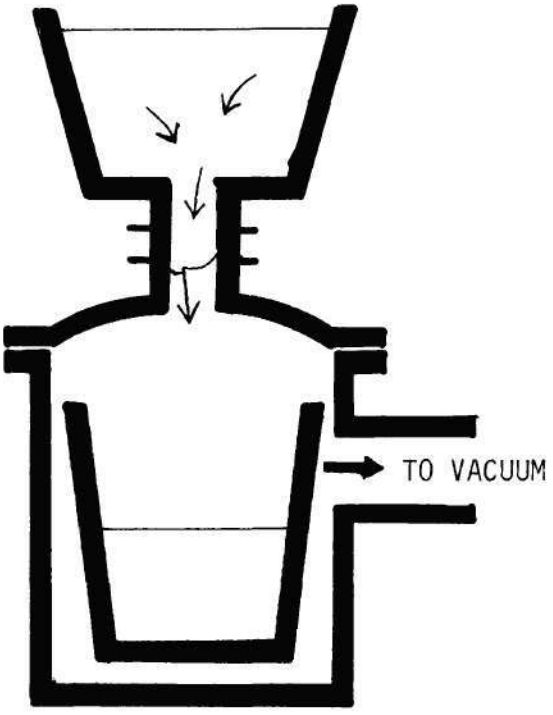


Figure 35. Stream Degassing Method.

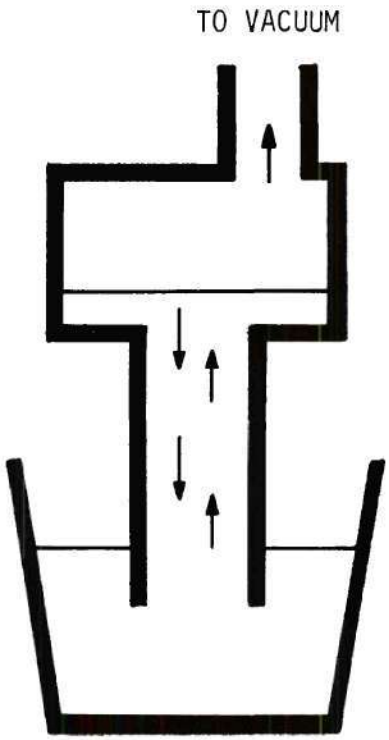


Figure 36. Ladle Suction Degassing Method.

sists of lowering a protrusion at the bottom of a vacuum chamber into a ladle of copper. A portion of the copper travels from the ladle up into the vacuum chamber where it is degassed. The vacuum chamber is then raised slightly and the degassed copper runs back into the ladle with the rest of the copper. This cycle is repeated several times, thereby progressively lowering the gas content. Mixing or stirring is automatically accomplished.

The continuous degassing of copper suggested by Dr. N. N. Engel[39] is based on degassing small amounts of copper at a time. The advantage in this approach is that only a relatively small vacuum pump is necessary to achieve a thorough degassing. The method delivers a constant stream of degassed metal suitable for continuous casting processes.

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